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# Seasonal nutrients variation, eutrophication pattern, and Chlorophyll *a* response adjacent to Guangdong coastal water, China

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Nutrients were the key biogenic elements for the primary production in coastal water, and the increase of nutrient concentration led to eutrophication and frequent occurrence of harmful algal blooms. However, the seasonal nutrients variation, eutrophication pattern, and Chlorophyll *a* (Chl-*a*) response adjacent to Guangdong coastal water were still scarcely. In this study, to clarity the seasonal nutrients variation, eutrophication pattern, and Chl-*a*, response adjacent to coastal water, the spatiotemporal dissolved inorganic nitrogen (DIN) and phosphorus (DIP) patterns and Chl-*a* were explored by field observation using 52 stations in the coastal waters of Guangdong Province during the dry (April and May), wet (July and August) and normal (October and November) seasons in 2020. The results showed that the variability of Chl-*a*, DIN and DIP were significantly different in seasons ($P<0.01$), and the mean concentrations of Chl-*a*, DIN and DIP were 11.97 ± 28.12 μg/L, 25.84 ± 35.72 μmol/L and 0.59 ± 0.71 μmol/L.Among them, the mean value of Chl-*a* increased significantly from 9.99 ± 9.84 μg/L in the dry season to 18.28 ± 38.07 μg/L in the wet season, and then decreased significantly to 7.65 ± 27.64 μg/L in the normal season.The mean DIN value decreased significantly from 30.68 ± 43.58 μmol/L in the dry season to 21.91 ± 35.45 μmol/L in the wet season, and then increased to 24.91 ± 26.12 μmol/L in the normal season. the mean DIP value decreased from 0.58 ± 0.73 μmol/L in the dry season to 0.48 ± 0.65 μmol/L in the wet season and then increased significantly to 0.70 ± 0.73μmol/L in the normal season. In addition, the DIN and DIP concentrations at most monitoring stations met the Grade II national seawater quality standards, and only a few monitoring stations fail to meet the Grade IV national seawater quality standard. The DIN/DIP ratios ranged from 2.05 to 259.47, with an average of 43.77 ± 41.01, far exceeding the Redfield ratio, indicating the presence of P limitation in the nearshore waters of Guangdong Province. Besides, the EI values in the coastal waters of Guangdong Province are higher at 0.00 and 82.51, with an average of 4.16 ± 10.90. DIN and DIP were significantly and positively correlated with COD in each season ($P<0.05$). Moreover, DIN/DIP showed significantly positive correlations with Chl-*a* in all seasons (P<0.01), indicating that high Chl-*a* concentrations could be sustained by the nutrients supply in marine ecosystems. Therefore, it is necessary to strengthen the integrated management of land and sea and effectively mitigate regional estuarine and coastal water eutrophication and harmful algal blooms.

KEYWORDS

**nutrients, eutrophication pattern, chlorophyll *a*, coastal water, Guangdong**

## 1 Introduction

The oceans cover 71% of the Earth's surface area, and marine primary productivity is an important foundation of marine ecosystems. Phytoplankton in the ocean are one of the primary producers of the ocean. They use light energy to absorb nutrients from seawater and convert inorganic carbon into organic carbon, while releasing oxygen, thus directly or indirectly providing the material base on which other organisms in the ocean depend. Chlorophyll *a* (Chl-*a*) in phytoplankton is an important indicator to monitor changes in phytoplankton abundance and also an important indicator of the degree of nutrient pollution of seawater. Therefore, accurate analysis and study of the variation of Chl-*a* in seawater plays a crucial role in exploring the phenomenon of eutrophication in the ocean. (Field et al., 1998; Falkowski et al., 2008; Lie et al., 2011; Aranguren-Gassis et al., 2019).

Nitrogen and phosphorus from seawater are essential nutrients for marine phytoplankton in coastal waters. At the same time, they are also the basis of marine primary productivity and the food chain.(Howarth, 2009; Butusov et al., 2013). Meanwhile, nitrogen and phosphorus in seawater are limiting nutrients for phytoplankton, and their concentration and composition directly affect the species, quantity and disteibution of phytoplankton. (Abell et al., 2010; Paerl et al., 2011; Paerl et al., 2016; Schindler et al., 2016; Smith et al., 2017; Yuan et al., 2018). The distribution and transformation of nitrogen and phosphorus elements in the ocean have been the main sources of nutrients in the ocean, including rivers, atmospheric deposition, and sediment release, and play a very important role in nutrient balance and dynamics (Liu J, et al., 2022). The growth of phytoplankton is closely related to the nutrient salts in seawater, and the concentration of Chl-*a* also changes with the nutrient salt concentration in seawater. Insufficient nutrient salts will limit the production of phytoplankton, leading to a subsequent decrease in the Chl-*a* concentration in seawater, which affects the primary productivity of the ocean; while too high a level of nutrient salt concentration tends to increase the Chl-*a* concentration, thus causing eutrophication and serious harm to the marine ecosystem.(Justi et al., 1995). At the same time, the nutrient ratio also has an effect on the concentration of Chl-*a* in seawater (Wang et al., 2015; Wang et al., 2017; Zou et al., 2022).With the development of human life science and technology production, the input of land-based sources of pollutants has an increasing impact on the marine environment, and one of the most serious problems facing mankind at present is the eutrophication of coastal waters (Philippart et al., 2007; Beusekom et al., 2019; Ibáñez and penuelas, 2019). Eutrophication of water resources refers to the phenomenon that under the influence of human activities, a large amount of nitrogen, phosphorus and other nutrients required by organisms enter slow-flowing water bodies such as lakes, rivers and bays, causing rapid reproduction of algae and other planktonic organisms, a decrease in dissolved oxygen in water bodies, deterioration of water quality, and the death of fish and other organisms in large quantities (Conley et al., 2009; Li et al., 2022). It is usually associated with an increase in nutrient concentrations in the water column (Hoyer et al., 2002; Mourão et al., 2020). Regionally, oceans with different characteristics also exhibit different nutrient distribution characteristics due to current current movements and biological activities (Pan et al., 2003). Meanwhile, Chl-*a* production and primary productivity of phytoplankton can directly reflect the degree of eutrophication in water bodies (Qin et al., 2013; Li et al., 2016).

Currently, eutrophication was one of the main issues in worldwide coastal waters. (Yu et al., 2018; Zhang C, et al., 2020). In addition, harmful algal blooms will persist in Chinese coastal waters because the water bodies are disturbed by nutrient imbalance (Zhen et al., 2017; Huang et al., 2018; Wu et al., 2022). It has been shown that, based on historical observations, eutrophication has led to a dramatic increase in microalgal biomass and a decrease in diatom-methanotrophic ratios in the East China Sea, especially in the spring; and that eutrophication has played an important role in multiple harmful algal bloom events in the Bohai Sea, both in the bays and near the estuaries (Zhou et al., 2022; Li et al., 2023; Wang et al., 2023). Thus, eutrophication is one of the most prominent environmental problems in China's coastal waters (Vaquer-Sunyer and Duarte, 2008; Li et al., 2013). The input of pollutants from land-based sources to offshore waters is increasing day by day (Niu et al., 2020). For example, the water quality of offshore waters in Bohai Bay in Tianjin is polluted, and the increase of land-based pollutants entering offshore waters along with surface runoff is the main reason (Guo et al., 2005; Liu et al., 2019); the water quality near the estuary in shallow waters of Liaodong Bay is poor (Pei et al., 2019); the distribution of pollutants in offshore waters in Shandong is increasing from the far shore to the near shore, and eutrophication is serious(Yang et al., 2020); the water quality condition of offshore seawater in Lianyungang, Jiangsu shows that the water quality condition in the region is seriously affected by human activities (Wang et al., 2011; Wang et al., 2022). The Yangtze estuary is not only the locomotive of economic development affecting China, but also a key area of coastal pollution (Cui and Xian, 2018). Although the problems caused by pollution of sediment, heavy metals, ecological environment, red tide and other major chemical pollutants in the nearshore coastal seawater of Guangdong Province have been widely reported in the literature (Zhang L, et al., 2020; Liu Y, et al., 2022), the eutrophication studies in Guangdong Province are mainly focused on the coastal waters of the Pearl River Estuary. (Huang et al., 2003; Shi et al., 2017; Chen et al., 2023), and the spatial and temporal distribution of nutrients and eutrophication of water bodies in the whole Guangdong Province coastal water are scarcely understood.

With the rapid social and economic development, human activities such as land-based pollutant discharge and marine aquaculture in coastal areas of Guangdong Province are expanding. The ecological and environmental problems associated with eutrophication are (Ke et al., 2023) still to be solved. In this paper, we analyze the survey data of Guangdong near-shore coastal areas in 2020 to understand the water quality of Guangdong near-shore waters by analyzing the observation data of three water seasons: normal season, wet season and dry season. Therefore, the objectives of this study are (1) to elucidate the spatial and temporal patterns of nutrients and Chl-*a* response associated with coastal waters of Guangdong Province, (2) to determine the degree of eutrophication by eutrophication index (EI), and (3) to identify the relationships between dissolved inorganic nitrogen (DIN), phosphorus (DIP), and EI and control factors in different seasons, (4) to explore the effect of seasonal changes in nutrients on Chl-*a*.The results of the study can provide basic data accumulation for the effective control of eutrophication marine environmental problems in local nearshore seawater in Guangdong Province, and provide scientific basis for the comprehensive management of nearshore coastal environment in Guangdong Province in the future.

# 2 Materials and methods

## 2.1 Study areas

Guangdong Province is located in the southern Nanling Mountains, along the South China Sea coast, bordering Guangxi, Hunan, Jiangxi, Fujian, Hong Kong, and Macau, and facing Hainan across the Qiongzhou Strait (Song et al., 2022). Meanwhile, Guangdong Province is located in the southeastern part of the coastal economic zone, south of the South China Sea, with a sea area of 419,300 square kilometers, making it a large marine economic province in China (Figure 1A). Located between latitude 20°09´~25° 31´ North and longitude 109°45´~117°20´ East, it has a vast land

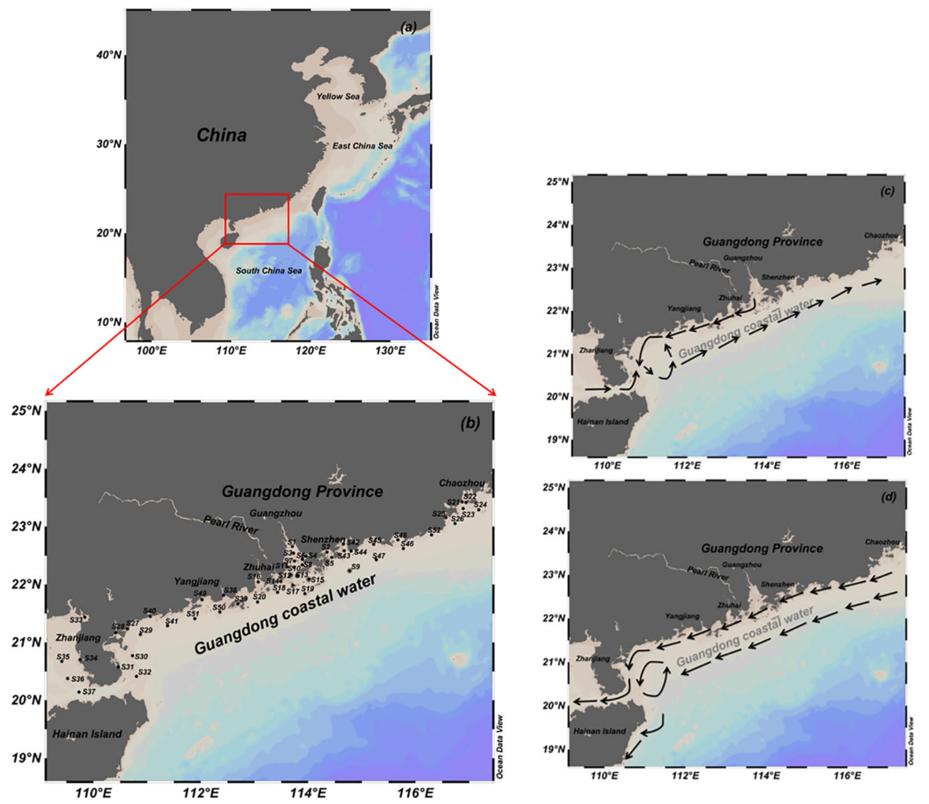


FIGURE 1
Research areas **(A)** and monitoring stations **(B)** in coastal waters of Guangdong Province, and the direction of ocean currents in summer **(C)** and winter **(D)**. (Wei et al., 2020).

area of 179,800km$^2$. The climate of the offshore waters of Guangdong Province belongs to the subtropical monsoon climate. The direction of the sea currents in the coastal waters of Guangdong Province changes in different seasons. Generally speaking, in summer, due to the influence of the monsoon, the currents mainly flow from south to north, while in winter, the monsoon is reversed, resulting in a corresponding change in the direction of the currents, which mainly blow from the north to the South China Sea (Figures 1C, D). In the spring and fall seasons, the alternation of the northeast monsoon and southwest monsoon brings about changes in the direction and strength of the currents, which may show a more complex distribution of flow direction and speed. However, the currents may also be affected by other factors, such as typhoons, tides, land runoff and so on (Qian et al., 2014; Wei et al., 2020). The total length of the mainland coastline is 4114km, and the marine resources are abundant. According to the Guangdong Yearbook, there are 714 species of marine organisms in Guangdong waters, including 187 species of phytoplankton, 319 species of zooplankton, 175 species of benthic and intertidal organisms, 24 species of reef-building stony corals, and 9 species of coral reef fish. Zhuhai, Guangdong Province, has 147 islands, one of the cities with more islands in China. since the 1970s, with the high economic development and population density of Guangdong, the degree of pollution of Guangdong's offshore waters has been increasing. Among them, the Pearl River estuary is the most polluted sea area, the rising trend of pollution is more obvious, and the seawater eutrophication is serious (Ke et al., 2022).

## 2.2 Data sources and laboratory analysis

Monitoring data from the Guangdong Provincial Department of Ecological and Environmental Protection (http://gdee.gd.gov.cn/) in 2020 for the offshore waters of Guangdong Province were the source of data for the analysis and study in this paper. Water flow seasons were sampled during the dry, wet and normal seasons in 2020 according to seasonal hydrological changes (Ministry of Environmental Protection of the People's Republic of China, 2002). April and May during the monitoring period represent the dry season, July and August represent the wet season, and October and November are the normal seasons. In order to ensure the comparability of data among the three water seasons, monitoring data from 52 common station monitoring stations were used in this paper (Figure 1B).

After the sample were collected, they were first filtered through acetate filter membrane with a pore size of 0.45 μm. The filters need to be rinsed with pure water before use (China National Standardization Management Committee, 2007). Water samples were frozen at - 20°C prior to chemical analysis. In this study, DIN included $NO_3^-$N, $NO_2^-$N, $NH_4^+$N, and $PO_4^{3}$–P was considered as DIP (Sun et al., 2021). In the laboratory analysis, where Chl-*a*, $NO_3^-$ N, $NO_2^-$N, $NH_4^+$N, and DIP were analyzed by Spectrophotometric method (Chen et al., 2016), sodium hypobromite oxidation method, diazo-diazo method, respectively. zinc- cadmium reduction method (Wang et al., 2022; Lu et al., 2023), and phosphorus-molybdenum blue method (Murphy and Riley, 1962; Mariko et al., 2018). The detection limit of Chl-*a* was 0.04 mg/L; the detection limit of $NO_3^-$ N, $NO_2^-$N and $PO_4^{3}$–P was 0.02 μmol/L; the detection limit of $NH_4^+$ N was 0.03 μmol/L.The relative standard deviations of the selected samples were determined by the standard colorimetric method described in the Specifications for Marine Investigations (China National Standardization Administration, 2007). The relative standard deviations (RSDs) of the selected samples were< 5% for repeated determinations (China National Standardization Administration, 2007). Details of the analytical methods, procedures and instrumentation in this study have been described in the Specifications for Marine Investigations (China National Standardization Administration Committee, 2007).

## 2.3 Data processing and statistical analysis

### 2.3.1 Water quality and eutrophication evaluation methods

According to the evaluation method of seawater quality, DIN and DIP pollution evaluation usually uses the single factor pollution index ($P_i$) method (Zhou and Cai, 1998; Ming et al., 2010). And its calculation formula is as follows:

$$P_i = C_i/S_i \tag{1}$$

Where (1): $C_i$ and $S_i$ are DIN and DIP measured data and Chinese national seawater quality standard values based on marine functional zoning, respectively. When $P_i$>1, it is regarded as exceeding the standard water quality, and the water body has been polluted; when $P_i$<1, it indicates that the water body is not polluted, and the degree of pollution of the water body increases with the increase of $P_i$ value.

In addition, to determine the number of monitoring stations with higher DIN and DIP pollution patterns in coastal waters in each season, the exceedance rate (%) was introduced, which is expressed as:

$$Over - \text{standard rate-} \% \text{-} = \frac{N_i}{\sum N_i} \times 100\,\% \tag{2}$$

Where (2): $N_i$ and $\sum N_i$ are the number of coastal water monitoring stations with high DIN and DIP concentrations in coastal waters of Guangdong ($P_i$ > 1) and the total number of monitoring stations by season, respectively (Ministry of Environmental Protection of the People's Republic of China, 2009).

In order to comprehensively evaluate the degree of eutrophication in the near-shore waters of Guangdong Province, this paper applies the integrated index method to calculate the eutrophication index (EI) of the surveyed waters based on DIN, DIP and COD survey data (Quan et al., 2005; Zou et al.,1983; Chen et al., 2016). And its calculation formula is as follows:

$$EI = \frac{C_{COD} \times C_{DIN} \times C_{DIP}}{4500} \times 10^6 \tag{3}$$

Where (3): $C_{COD}$, $C_{DIN}$ and $C_{DIP}$ are the concentrations of COD, DIN and DIP respectively (unit is mg/L). When the index

EI≥1, it means that the sea water body is eutrophic, and the larger the EI value is, the more serious the eutrophication is.

### 2.3.2 Data processing and analysis

This paper uses the geographic information system ArcGIS (10.2) to draw a schematic diagram of monitoring stations in Guangdong Province; uses Excel software to process data, and Ocean Data View (4.0) software to draw spatial distribution maps of Chl-*a*, DIN, DIP concentration, nitrogen/phosphorus ratio N/P and eutrophication index EI; and uses Origin (2021) software to draw coastal Guangdong Province monitoring stations of the water quality exceedance rate, and the correlation heat map of the relationship between DIN, DIP and EI and control factors; The data were first tested for normal distribution in SPSS software, ($P<0.05$) and the results obtained clearly did not conform to normal distribution, and then non-parametric tests (Kruskal-Wallis test) were used to assess the significant differences in seasonal variations, as well as Spearman's correlation significance test for the impact factors of nutrients to test the statistical differences in the data.The data in this paper are expressed using the arithmetic mean ± standard deviation (Mean ± SD).

# 3 Results

## 3.1 Seasonal Chl-*a* variation in coastal waters of Guangdong Province

There were significant seasonal differences in Chl-*a* concentrations in coastal waters of Guangdong Province ($P<0.01$). During the survey period, the average concentration of Chl-*a* in the coastal waters of Guangdong Province was 11.97 ± 28.12 μg/L, with a concentration range of 0.18-218.40 μg/L.From a temporal perspective, the average concentration of Chl-*a* in the three water seasons was 9.99 ± 9.84 μg/L in the dry season, with a concentration range of 1.22-36.04 μg/L; The average concentration of Chl-*a* in the wet season was 18.28 ± 38.07 μg/L, with a concentration range of 0.18-218.40 μg/L; The average concentration of Chl-*a* in the normal season was 7.65 ± 27.64μg/L, and the concentration range was 0.22-202.80μg/L.Upon comparison, the average Chl-*a* concentration was the highest in the nearshore waters of Guangdong Province during the wet season, and its Chl-*a* concentration showed a trend of increasing and then decreasing from the dry season to the normal season. In terms of spatial distribution, during the dry season, the highest Chl-*a* concentration was found in the waters near Zhanjiang City, at Station 33, at 36.04 μg/L. This was followed by the waters near Zhuhai City (Figure 2A). During the wet season, Chl-*a* concentrations were higher in Zhanjiang City, Yangjiang City and the outer locations of the Pearl River Estuary, which highest Chl-*a* concentrations were found at Station 8 near Shenzhen City with up to 218.40 μg/L (Figure 2B). During the normal season, the waters with high Chl-*a* concentrations were mainly concentrated near Yangjiang City, where the highest recorded in the season occurred at Station 49. While all other areas were at low levels (Figure 2C).

## 3.2 Spatiotemporal variation of DIN concentration in coastal waters of Guangdong Province

There were significantly seasonal differences in DIN concentrations in coastal waters of Guangdong Province ($P<0.01$). During the survey period, the average concentration of dissolved inorganic nitrogen DIN in the coastal waters of Guangdong Province was 25.84 ± 35.72μmol/L, with a concentration range of 0.29-231.21μmol/L. From the perspective of time, in the three water seasons, the average concentration of DIN in the dry season was 30.68 ± 43.58μmol/L, and the concentration range was 0.29-231.21μmol/L; the average concentration of DIN in the wet season was 21.91 ± 35.45μmol/L, and the concentration range was 0.35-127.30μmol/L; the average concentration of DIN in the normal season was 24.91 ± 26.12μmol/L, and the concentration range was 2.11-99.21μmol/L. By comparison, the average concentration of DIN in the dry season was higher in the coastal waters of Guangdong Province. However, the distribution of DIN concentration from the dry season to the normal season showed a trend of first decreasing and then increasing. From the perspective of spatial distribution, the horizontal distribution of DIN concentration in all three seasons showed decreasing near-shore to far-shore, with the Pearl River port as the center and decreasing outward concentration (Figure 3). During the dry period, the high DIN concentration was mainly concentrated in the location of the Pearl River estuary, and the highest level was recorded at the Station 1 in its nearby waters (Figure 3A); while in the wet season, the DIN concentration at each station was generally lower than that in the dry season. During the period of wet water, in addition to the high DIN pollution concentration in the Pearl River Estuary, the DIN concentration in the sea near Zhuhai, Jiangmen, Yangjiang and Zhanjiang is also high compared to other stations (Figure 3B). In the normal season, the distribution of DIN concentration is basically the same as that in the wet season, but the distribution range of high DIN concentration is much smaller than that in the wet season (Figure 3C).

## 3.3 Spatial and temporal variation of DIP concentration in coastal waters of Guangdong Province

There were significantly seasonal differences in DIP concentrations in coastal waters of Guangdong Province ($P<0.01$). During the survey period, the average concentration of dissolved inorganic phosphorus DIP in the coastal waters of Guangdong Province was 0.59 ± 0.71μmol/L, with a concentration range of 0.01-3.65μmol/L. From a temporal perspective, in the three water seasons, the average concentration of DIP in the dry season was 0.58 ± 0.73μmol/L, with a concentration range of 0.09-3.23μmol/L; The average concentration of DIP during the wet season was 0.48 ± 0.65μmol/L, with the concentration range of 0.06-3.10μmol/L; the average concentration of DIP during the normal season was 0.70 ± 0.73μmol/L, with the concentration range of 0.01-3.65μmol/L. By comparison, the average concentration of DIP during the normal season was the highest in the coastal waters of Guangdong Province, and the concentration of DIP from the dry season to the normal

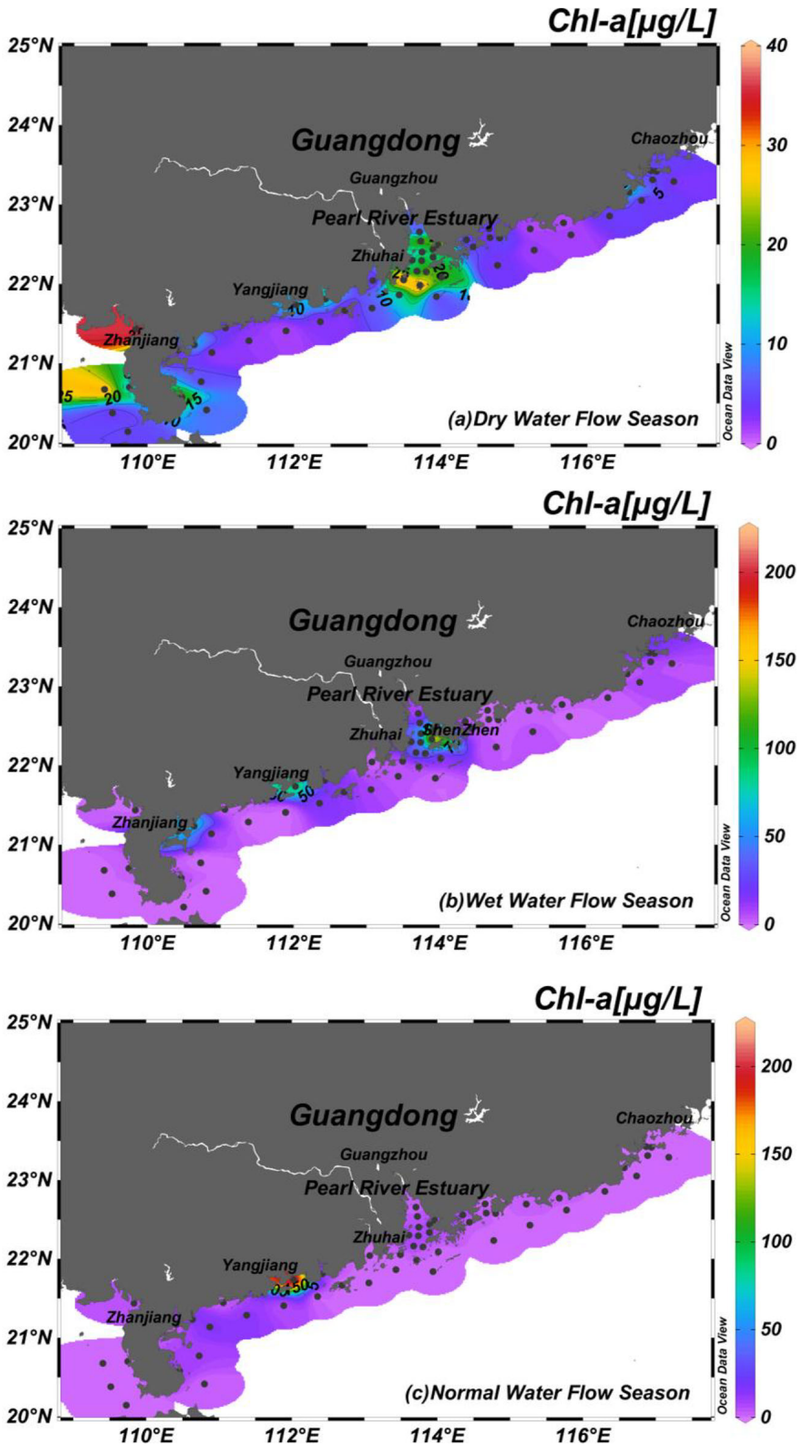


FIGURE 2
Spatiotemporal variation of Chl-*a* concentration during the dry season **(A)**, wet season **(B)**, and normal season **(C)** in the Guangdong coastal water.

season showed a first decrease and then increase. The DIP concentration from the dry season to the normal season showed a trend of decreasing and then increasing, and the DIP concentration in the normal was higher than the DIP concentration in the dry season. In the dry season, the high DIP concentrations were mainly concentrated in the waters near the Pearl River Estuary and Zhanjiang City (Figure 4A); while in the wet season, the DIP concentrations at all stations were generally lower than those in the dry season (Figure 4B). During the normal period, the highest value of DIP concentration appeared in the sea near Zhanjiang City, where the highest record was obtained at Station 28, up to 3.65 μmol/L, followed by the location of the Pearl River Estuary (Figure 4C).

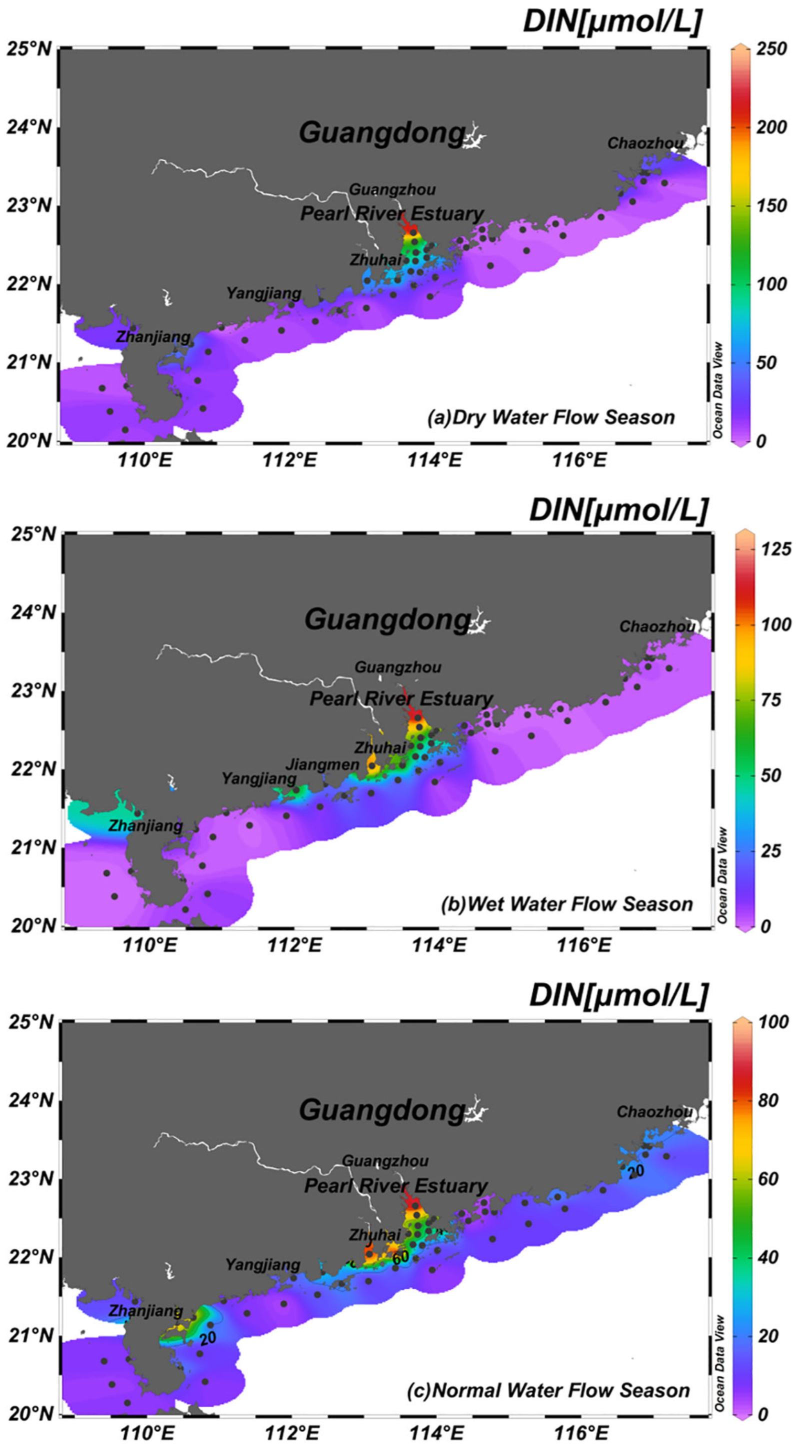


FIGURE 3
Spatiotemporal variation of DIN concentration during the dry season **(A)**, wet season **(B)**, and normal season **(C)** in the Guangdong coastal water.

## 3.4 Spatial and temporal variation of DIN/DIP in coastal waters of Guangdong Province

There was a significant difference in DIN/DIP in seasonal coastal waters of Guangdong Province ($P<0.05$). During the survey period, the DIN/DIP in the nearshore waters of Guangdong Province fluctuated between 2.05 and 259.47 with a mean value of 43.77 ± 41.01. The mean value of DIN/DIP in the coastal waters of Guangdong Province decreased from 49.52 ± 41.50 in the dry season to 37.13 ± 42.38 in the wet season, and then increased significantly to 44.65 ± 38.91 in the normal season. The DIN/DIP ranged from 3.05 to 259.47 during the dry season. The DIN/DIP ranged from 2.05 to 231.02 during the wet season and from 15.73 to

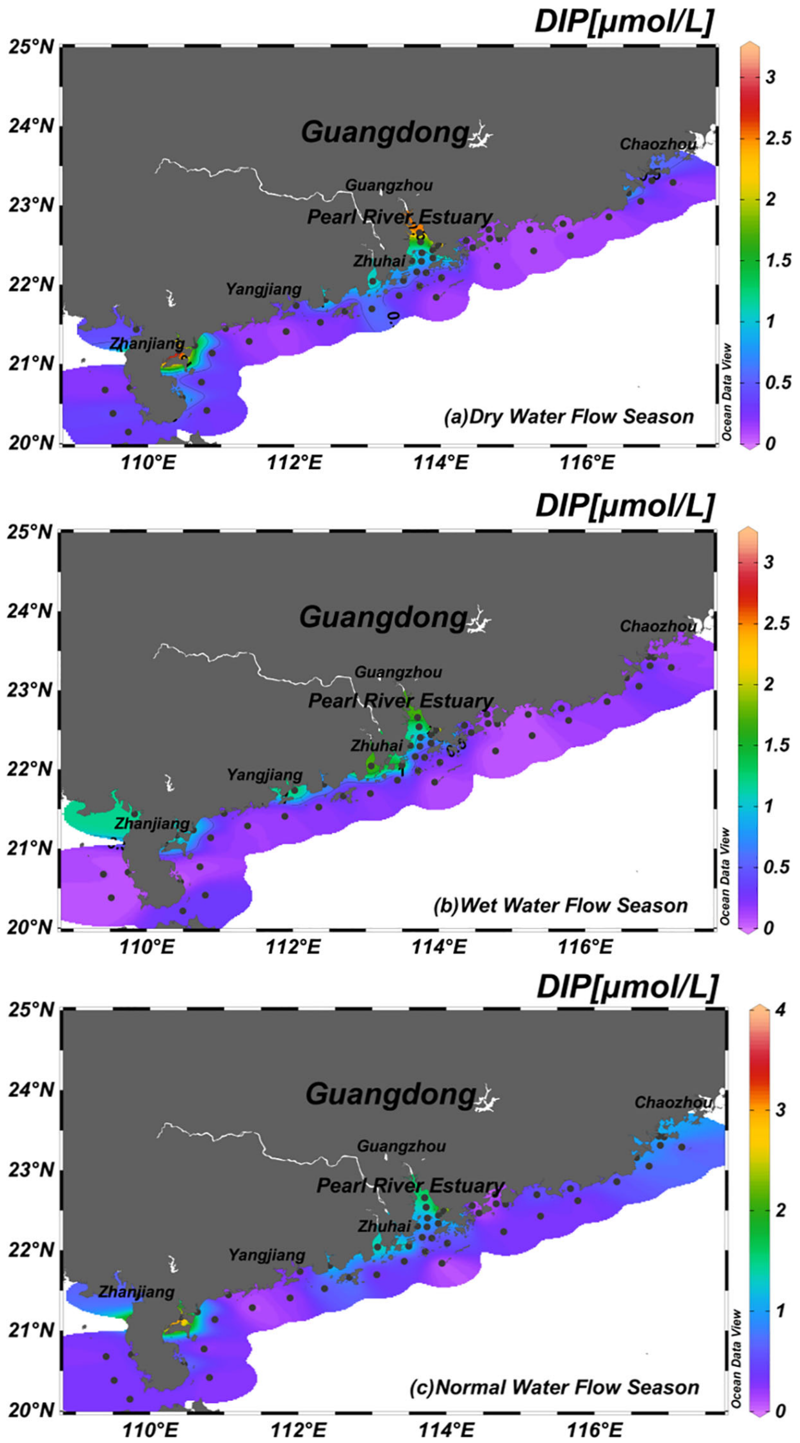


FIGURE 4
Spatiotemporal variation of DIP concentration during the dry season **(A)**, wet season **(B)**, and normal season **(C)** in the Guangdong coastal water.

238.04 during the normal season. Spatially, there were some differences in DIN/DIP in the nearshore waters of Guangdong (Figure 5). During the dry season, the proportion of DIN/DIP distribution was larger near the Pearl River Estuary and smaller away from the estuary. The highest value of DIN/DIP was found at the monitoring station near Shenzhen, which was Station 7, with a high value of 259.47. (Figure 5A). During the period of wet water, the range with higher DIN/DIP ratio was the sea area near Zhuhai city (Figure 5B). During the normal season, the range of higher DIN/DIP ratio is different from the dry and wet seasons, it occurs far from the Pearl River Estuary, and the highest record occurs near Shenzhen, specifically at Station 2, where the DIN/DIP is 238. 04. (Figure 5C).

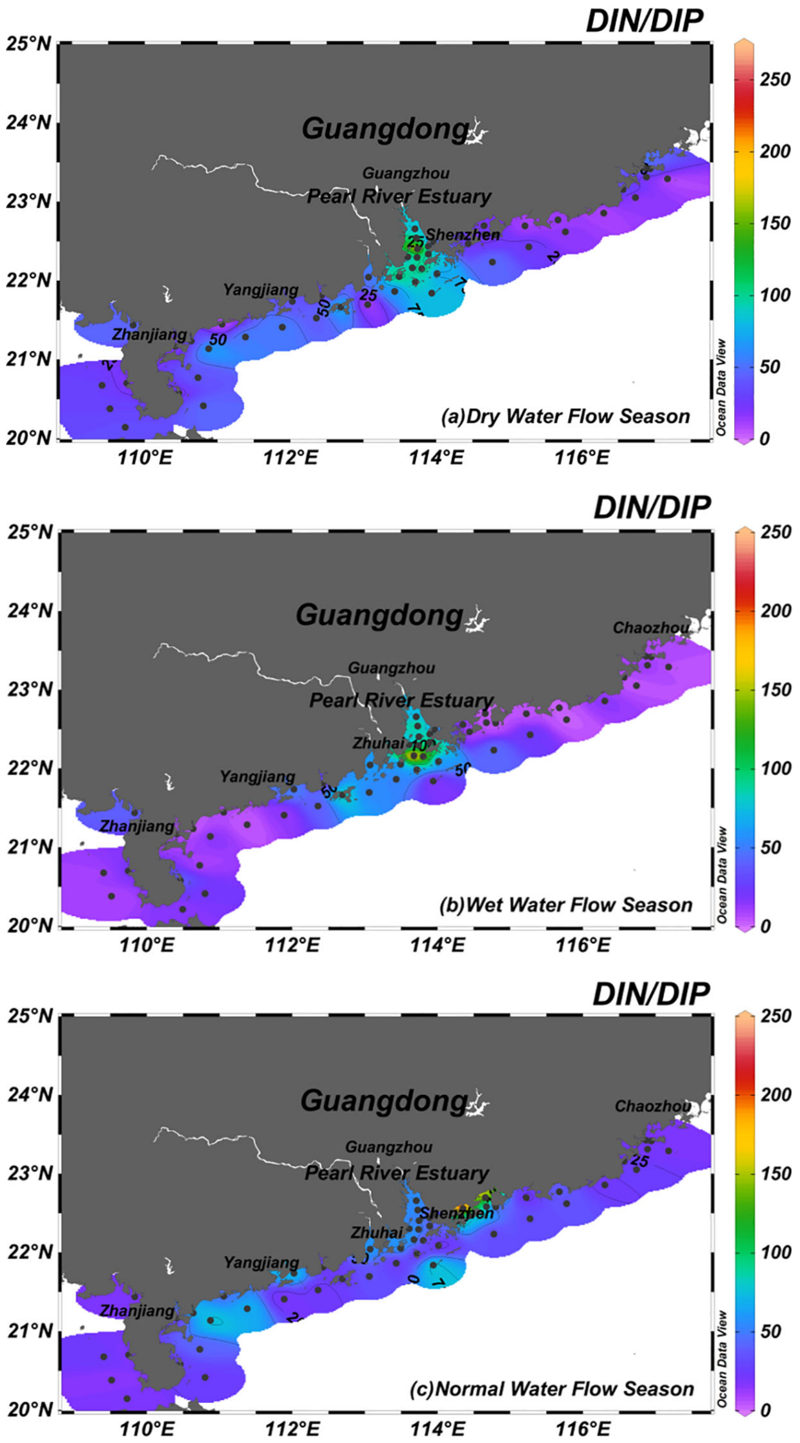


FIGURE 5
Spatiotemporal variation of DIN/DIP during the dry season **(A)**, wet season **(B)**, and normal season **(C)** in the Guangdong coastal water.

## 3.5 Spatial and temporal variation of EI in coastal waters of Guangdong Province

There were significantly seasonal differences in EI in coastal waters of Guangdong Province ($P<0.05$). During the survey period, the average EI of the three water periods in the nearshore waters of Guangdong was 4.16 ± 10.90, and the minimum and maximum values of EI were 0.00 and 82.51, respectively. The EI of the nearshore waters of Guangdong showed a decreasing trend from the dry season to the normal season. During the dry season, the range of EI in the coastal waters of Guangdong was 0.00-82.51, with a mean value of 5.93 ± 15.44; During the wet season, the range of EI in the coastal waters of Guangdong was 0.00-34.77, with a mean value of 3.93 ± 8.93; During the normal season, the range of EI in the coastal waters of Guangdong was 0.00-31.87, with a mean value of 2.63 ± 6.09; spatially, the EI in the offshore waters of Guangdong showed significant differences (Figure 6). During the dry season, the EI was higher near the Pearl River Estuary, and the further away from the Pearl River Estuary, the lower the EI was (Figure 6A). During the wet season, its EI is smaller than that in the dry season. Except for the stations near the Pearl River Estuary, the EI of the waters near Zhanjiang City, Yangjiang City, Zhongshan City, Shenzhen City and Zhuhai City is relatively large (Figure 6B). Normal water period, its highest EI value appeared in the sea near Zhanjiang City, which is the Station 28 to obtain the highest record of this water period, up to 31.87, followed by higher EI in the sea near Zhongshan City and Zhuhai City (Figure 6C).

## 3.6 Seasonal relationships between DIN, DIP, EI and environmental factors

The Spearman correlation coefficients showed that the influencing factors of DIN, DIP and EI showed some seasonal variations in the

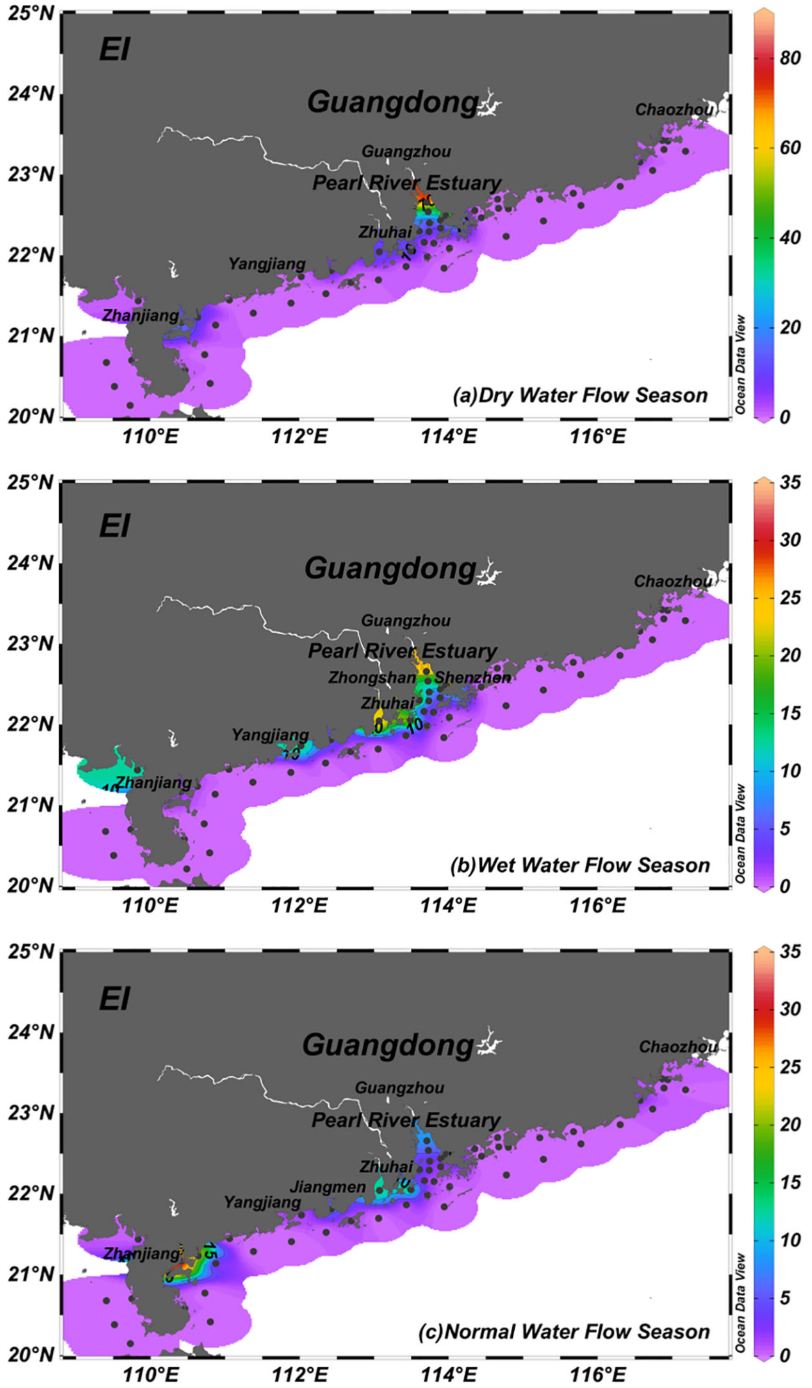


FIGURE 6
Spatiotemporal variation of EI during the dry season **(A)**, wet season **(B)**, and normal season **(C)** in the Guangdong coastal water.

nearshore waters of Guangdong Province (Figure 7). In the dry and wet water periods, DIN, DIP, EI and Chl-*a* were significantly positively correlated (P<0.01); while in the normal season (Figure 7C), EI and Chl-*a* were positively (Figures 7A, B) correlated (P<0.05), but DIN, DIP and Chl-*a* were not significantly correlated. In the three water periods, DIN, DIP, and EI were significantly negatively correlated with pH (P<0.01). In the wet season, DIN was significantly positively correlated with DO (P<0.05), except for the other water periods, the concentrations of DIN and DO were not correlated. Meanwhile, there was no significant correlation between DIP, EI and DO. DIN, DIP and EI were positively correlated with COD in all three water periods (P<0.05). The concentrations of DIN, DIP and EI were significantly positively correlated in all three water periods (P<0.01). In addition (Figure 7D), DIN, DIP and EI were significantly and positively correlated with suspended matter in all three water periods (P<0.01). DIN, DIP, and EI were positively correlated with petroleum during the

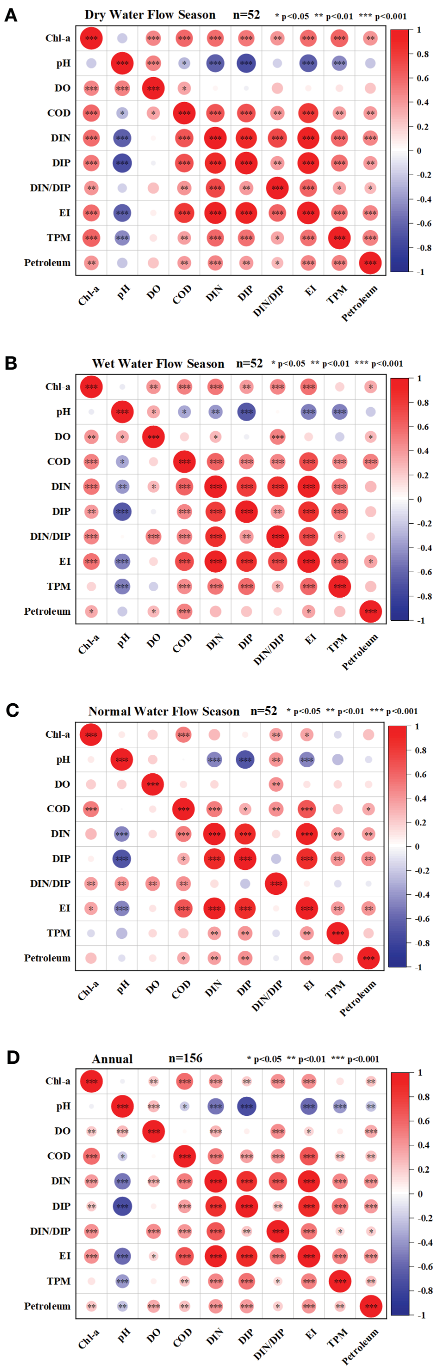


FIGURE 7
Correlation relationships among DIN, DIP, EI and environmental factors during the dry season **(A)**, wet season **(B)**, normal season **(C)** and annual **(D)** in Guangdong coastal waters. (n = 52).

dry and normal water periods (P<0.05). In addition, DIN/DIP was significantly and positively correlated with Chl-*a* in all three water periods (P<0.01) (Figure 7D).

# 4 Discussion

## 4.1 Comparison with global estuaries and coastal water

The data of nutrient content, DIN/DIP and EI are listed in this paper. However, in order to further elucidate the pollution levels of nutrients in the nearshore waters of Guangdong Province, it is necessary to compare the results of this study with those of other studies (Table 1). The DIN concentrations in the nearshore waters of Guangdong Province were higher than those previously reported in Hainan Island, Kaohsiung Harbor, Laizhou Bay, Qinzhou Gang, Weizhou Island, and Lianyungang (Chen et al., 2016; Ning et al., 2020; Zhang P, et al., 2020; Lu et al., 2022; Wang et al., 2022; Zhang M, et al., 2022), but lower than those in the Changjiang River, Mississippi River (Turner et al., 2007; Cui and Xian, 2018). However, the DIP concentrations were higher than those in Laizhou Bay, Weizhou Island and Lianyungang (Ning et al., 2020; Wang et al., 2022; Zhang M, et al., 2022), but lower than those in Kaohsiung Harbor, Qinzhou Gang, the Changjiang River and Mississippi River (Turner et al., 2007; Chen et al., 2016; Cui and Xian, 2018; Lu et al., 2022). The DIN/DIP was higher than the previously investigated Qinzhou Gang, Weizhou Island, Lianyungang, and Mississippi River (Turner et al., 2007; Ning et al., 2020; Lu et al., 2022; Wang et al., 2022), but lower than Laizhou Bay and the Changjiang River (Cui and Xian, 2018; Zhang M, et al., 2022). EI is higher than previously reported for Hainan Island, Kaohsiung Harbor Laizhou Bay, Lianyungang (Chen et al., 2016; Zhang P, et al., 2020; Wang et al., 2022; Zhang M, et al., 2022) and lower than the Changjiang River (Cui and Xian, 2018). In addition, the results showed that the DIN pollution level in offshore waters of Guangdong Province in 2020 was higher compared with other river estuaries, and the pollution level of DIP concentration is not low. And in general, the pollution level of DIN is higher than that of DIP. Therefore, DIN/DIP is much higher than 16 and higher than the DIN/DIP values of most other rivers. Besides, the mean value of EI is much lower than the Changjiang River and higher than other estuaries.

## 4.2 Seasonal DIN and DIP change pattern and eutrophication degree

According to the survey results, compared with the seawater quality standard, the percentage of the number of monitoring stations with DIN concentration exceeding the Grade IV seawater quality standard (DIN ≤ 35.71μmol/L) to the total number of monitoring stations was 28.85%, 19.23% and 23.08% in the dry season, wet season and normal season respectively (Figure 8A). In general, the level of DIN pollution in offshore waters of Guangdong Province is small. Mainly, the DIN concentration of most monitoring stations in the coastal waters of the Pearl River Estuary cannot reach the seawater quality standard of Grade IV or above (Shen et al., 2022), indicating that the coastal area of the Pearl River Estuary is seriously polluted. With the rapid socio-economic development, human activities such as land-based pollutant discharges, marine aquaculture and port shipping along the Pearl River Estuary are increasingly expanding, making the rivers along the Pearl River Estuary carry more nutrients. As a result, DIN concentrations at several monitoring stations in the area exceeded seawater quality standards (Li et al., 2020; Qian et al., 2022). In addition, DIN concentrations were highest during the dry season. Compared to the dry season, the average DIN concentrations in both the wet and normal season were significantly

TABLE 1 Comparison of the nutrient concentrations, EI and DIN/DIP in the coastal waters of Guangdong with global estuaries and coastal water.

| Region | Time | DIN (μmol/L) | DIP (μmol/L) | DIN/DIP | EI | References |
|---|---|---|---|---|---|---|
| Hainan Island | 2016 | 8.14 (0.57-27.5) | – | – | 0.21 (0.00-3.94) | Zhang P, et al., 2020 |
| Kaohsiung Harbor | 2012 | 11.43 ± 7.86 (2.86-34.29) | 5.81 ± 2.26 (1.94-15.16) | – | 2.24-139.39 | Chen et al., 2016 |
| Laizhou Bay | 2021 | 9.22-54.69 | 0.05 ± 0.04-0.32 ± 0.79 | 130.65 | 0.24-3.21 | Zhang M, et al., 2022 |
| Qinzhou Gang | 2011-2017 | 20.1 ± 17.2 | 1.0 ± 0.9 | 43 ± 46 | – | Lu et al., 2022 |
| Weizhou Island | 2018 | 3.84 | 0.24 | 16.0 | – | Ning et al., 2020 |
| Lianyungang | 2016 | 10.71 | 0.42 | 15.1 (1.6-55) | 0.6 (0.1-7.2) | Wang et al., 2022 |
| the Changjiang River | 2014 | 118.4 | 1.3 | 91.1 | 11.0 | Cui and Xian, 2018 |
| Mississippi River | 1997-2006 | 99.6 | 2.6 | 38.31 | – | Turner et al., 2007 |
| Guangdong coastal water | 2020 | 25.84 ± 35.72 (0.92-231.21) | 0.59 ± 0.71 (0.01-3.65) | 43.77 ± 41.01 (2.05-259.47) | 4.16 ± 10.9 (0.00-82.51) | This study |

"—" indicated not detected.

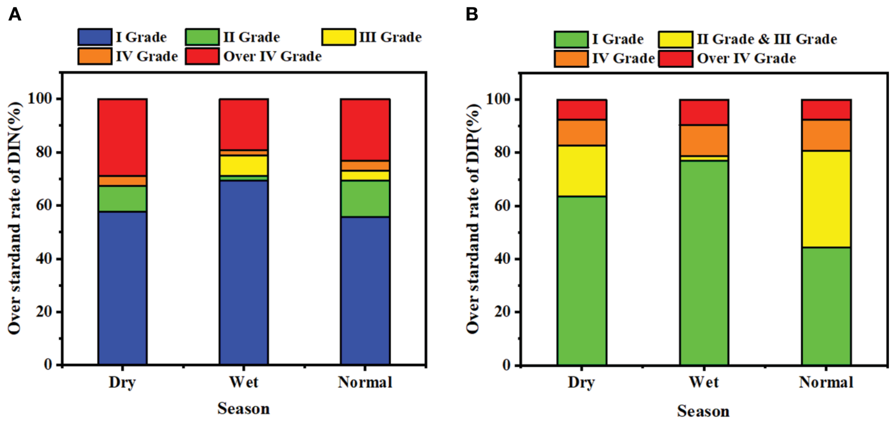


FIGURE 8
Over-standard rate of DIN **(A)** and DIP **(B)** in coastal water quality monitoring stations of Guangdong Province.

lower, because July and August are the rainy season, a high typhoon season, and constantly affected by the intrusion of rainwater, and the resuspended nutrients are quickly diluted.In addition, the temperature in the coastal water gradually increases and there is sufficient light, which is the peak period for algal growth during summer. As the temperature meets the conditions for rapid algal growth, the algae can absorb a large amount of nutrients from the water body while growing, resulting in a relatively low average DIN concentration during the wet period (Ke et al., 2022).

Compared with the national seawater quality standard, the percentage of the number of monitoring stations with DIP concentration exceeding the Grade IV seawater quality standard (DIP ≤ 1.45μmol/L) to the total number of monitoring stations was 7.69%, 9.62% and 7.69% in the dry season, wet season and normal season respectively (Figure 8B). In general, the level of DIP pollution in the offshore waters of Guangdong Province is small, and the DIP concentrations at most monitoring stations meet the seawater quality standard of Grade IV or higher, but there are still individual stations that do not meet the Grade IV standard. The average concentration of DIP is lowest during the wet season, which may be related to the frequent rainy season in July and August, when rainwater replenishes the sea and dilutes the concentration of DIP, or it may be caused by phytoplankton absorbing large amounts of nutrients from the seawater after heavy typhoon rains (Herbeck et al., 2011). The peak of DIP concentration occurs during the normal water period, which is due to the input of fresh water, domestic sewage and industrial wastewater from rivers with greater influence.

## 4.3 Key environmental factors affecting nutrient concentrations and composition in coastal waters of Guangdong Province

DIN and DIP were significantly negatively correlated with pH in all seasons (P<0.01). With the rapid development of industry in coastal areas, it has led to a great increase in the amount of $CO_2$ emitted into the atmosphere. The seawater absorbed a large amount of $CO_2$ from the air, which led to a decrease in the pH of seawater and the phenomenon of ocean acidification (Queré et al., 2014; Stocker, 2014; Rees et al., 2017). However, DIN and DIP were significantly and positively correlated with suspended matter in all seasons (P<0.01), which may be due to the fact that suspended matter in organic pollutants from land-based runoff carries a large amount of DIN and DIP. DIN and DIP were significantly and positively correlated with Chl-*a* in the dry and wet seasons (P<0.01), which may be due to the input of pollutants from land-based sources, promoting the rapid growth of phytoplankton (Han et al., 2023). DIN, DIP and COD are important indicators for evaluating coastal water quality (Ministry of Environmental Protection of the People's Republic of China, 1997) (Tu et al., 2022). In addition, DIN and DIP were significantly and positively correlated with COD in each season (P<0.01) because surface runoff in each season carried a large amount of pollutants of terrestrial origin, which provided a large amount of inorganic and nutrients for a large number of phytoplankton in the water column. DIN and DIP were significantly and positively correlated (P<0.01) with petroleum species during the dry and normal season, probably because DIP in surface seawater has the same source and fate as petroleum hydrocarbons.

Nutrients are important for the growth of phytoplankton. Phytoplankton in the ocean take up nutrients from seawater in a certain ratio, and this constant ratio becomes the Redfield (Turner et al., 2003). Under normal conditions, N:P is about 16. During the survey period, DIN/DIP values ranged from 2.05 to 259.47, with a mean value of 43.77 ± 41.01, which is much higher than the Redfield ratio. And DIN/DIP was significantly and positively correlated with Chl-*a* (p<0.01). High Chl-*a* concentrations can reflect the changes of nutrient content in marine ecosystems, and the extremely strong correlation between DIN/DIP and Chl-*a* indicates that the imbalance of nutrient ratios in coastal waters of Guangdong Province has led to the occurrence of harmful algal blooms, thus exacerbating the eutrophication phenomenon (Schlüter et al., 2000; Qiao et al., 2017). The DIN/DIP ratios in the dry and normal seasons were higher than those in the wet season, which was caused by the higher DIN concentration and relatively lower DIP concentration in the dry and normal season. As can be seen from Figure 5, the DIN/DIP values at the location of the Pearl River

Estuary were significantly higher, up to 259.47, indicating a serious imbalance in the nutrient composition of the offshore waters of the Pearl River Estuary, and the phenomenon of nutrient imbalance indicated that the discharge of industrial wastewater, domestic sewage and agricultural fertilizers near the Pearl River Estuary had a dynamic effect on the DIN/DIP values of the coastal waters. The eutrophication of nearshore water bodies in Guangdong Province is likely to continue due to the continued disturbance of nutrient ratios in these bodies (Wang et al., 2021).

### 4.4 Suggestions for effective mitigation of eutrophication in coastal waters of Guangdong Province

With rapid socio-economic development and rapid population growth, industrialization and urbanization have accelerated, human pursuit of material culture has been elevated and the scope of activities has been expanded, leading to a gradual increase in the discharge of nutrients imported from outside into water bodies. Under the implementation of the 14th Five-Year Plan for Marine Ecological Protection of Guangdong Province (Department of Ecological Environment in Guangdong Province, 2022), land-based pollutant inputs are reduced to improve water quality according to the characteristics of the near-shore waters of Guangdong Province.Combining the concentrations of Chl-*a*, DIN, DIP, and the DIN/DIP stoichiometry results, we found that the eutrophication of coastal waters in Guangdong Province is low, but the eutrophication problem is still prominent in local waters, especially in the Pearl River Estuary and the waters near Zhanjiang City (Ke et al., 2023). To reduce the eutrophication in coastal waters of Guangdong Province, firstly, numerical nutrient criteria for estuaries and adjacent coastal waters should be developed (Wu et al., 2010; Huo et al., 2018; Yang et al., 2019; Xie et al., 2021; Zhang P, et al., 2022). The application of nutrient standards is not only an effective measure to prevent eutrophication of water bodies, but also a scientific basis for comprehensive monitoring, evaluation and management of nutrients in estuaries. The government should strengthen the comprehensive control of eutrophic waters and the management related to the discharge of river pollutants into the sea. In the time scale, we need further monitor nutrients and Chl-*a* response in the ocean for a long time. Besides, considering the spatial and temporal differences of EI, it is necessary to investigate and analyze Chl-*a* and nutrients according to their distribution characteristics at different locations and times, and to implement suitable management measures.In addition, the publicity of river pollution prevention and control should be strengthened to raise citizens' awareness of coastal environmental protection participation. Integrated land and sea management of coastal water quality should be introduced in the future to control river and coastal water quality efficiently (Zeng-Lin et al., 2012; Gao et al., 2022).

## 5 Conclusion

Exploring the biogeochemical processes of nitrogen and phosphorus in the coastal waters of Guangdong Province is key to developing countermeasures to mitigate eutrophication. This study focuses on the spatial and temporal patterns of nutrients, their composition and their effects on mitigating eutrophication in the offshore waters of Guangdong Province. The results showed that the nutrients in 2020 showed seasonal variations, with DIN being highest in the dry season and DIP being highest in the normal season. In all seasons of the survey, DIN and DIP pollution levels were more severe in the vicinity of the Pearl River Estuary and Zhanjiang Bay than the other coastal water. Overall, based on the Redfield values, it can be seen that DIN concentrations are higher than DIP concentrations, indicating the presence of P limitation in the nearshore waters of Guangdong Province. The eutrophication index of seawater surface layer was significantly different among the three water seasons. The mean value of eutrophication index in the dry season was higher than that in the wet and normal seasons. In addition, nutrients and EI showed significantly positive correlations with COD($P<0.05$), as well as DIN/DIP was significantly and positively correlated with Chl-*a* ($p<0.01$), which indicated a direct relationship between eutrophication in the water column and the high input of nutrients. Therefore, controlling the input of total nitrogen and total phosphorus from land-based sources can effectively alleviate the eutrophication in the local coastal areas of Guangdong Province. In addition, harmful algal blooms may persist near the coastal waters of Guangdong Province due to the severely imbalanced nutrient ratios in the coastal water. Therefore, further research is needed on how to bring the heavily polluted coastal waters up to the relevant nutrient standards and ratios so as to effectively mitigate eutrophication and suppress harmful algal blooms.

## Data availability statement

The original contributions presented in the study are included in the article/supplementary materials. Further inquiries can be directed to the corresponding author.

## Author contributions

Conceptualization, PZ. Methodology, PZ and YH. Software, YH and FX. Validation, YH and FX. Formal analysis, YH and FX. Writing-original draft preparation, YH and PZ. Writing-review and editing, YH and PZ. Visualization, PZ, LZ and JZ. Supervision, PZ, LZ and JZ. Project management, PZ, LZ and JZ. Funding acquisition, PZ, LZ and JZ. All listed authors made substantial, direct, and intellectual contributions to the work and are approved for publication.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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