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Seasonal characteristics of nutrient and nutrient structure in the Yangtze River estuary

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Abstract: This data article aimed to evaluate the influencing mechanisms of the nutrients and the level of eutrophication in the Yangtze River estuary. The seasonal characteristics of nutrients (dissolved inorganic nitrogen (DIN), $\text{SiO}_3^{2-}\text{-Si}$, and PO_4^{3-}P) in the seawater of the Yangtze River estuary were analyzed by conducting surveys in spring and summer of 2019. The findings revealed that the concentrations of all nutrient at the surface and bottom layers were lower in spring compared to summer. $\text{NO}_3^{-}\text{-N}$ was typically the major form of DIN. Runoff was identified as the primary source of DIN and $\text{SiO}_3^{2-}\text{-Si}$, while PO_4^{3-}P originated from a various sources. The $\text{SiO}_3^{2-}\text{-Si}/\text{PO}_4^{3-}\text{P}$ and $\text{DIN}/\text{PO}_4^{3-}\text{P}$ values in the surface and bottom layers during the spring and summer were higher than the Redfield values, indicating an imbalanced nutrient distribution. Furthermore, discrepancies were observed in the distributions of $\text{DIN}/\text{PO}_4^{3-}\text{P}$, $\text{SiO}_3^{2-}\text{-Si}/\text{DIN}$, and $\text{SiO}_3^{2-}\text{-Si}/\text{PO}_4^{3-}\text{P}$ in the Yangtze River estuary. Through an examination of the ratio of $\text{DIN}/\text{PO}_4^{3-}\text{P}$ absorbed by phytoplankton, PO_4^{3-}P was identified as a potential limiting factor for nutrition in the sea area of the Yangtze River estuary during spring and summer. The Eutrophication Index (E) values for both spring and summer were found to be higher than the eutrophication threshold, indicating severe eutrophication in the studied sea area.

Introduction

Nutrients are necessary components for the growth and reproduction of marine phytoplankton in seawater, and serve as raw material for primary productivity and the food web. According to LIU (2011), the distribution and variation in nutrient concentration are directly related to the abundance of bacteria, populations of bacteria, phytoplankton, zooplankton, and other organisms in the estuary, as well as the resource, horizontal transportation, vertical mixing, and interface dynamics process of the sediment. The distribution and variation in nutrient content have a direct impact on the primary productivity and biological resources of the sea and serve as good indicators of marine environmental pollution and ecosystem changes. The characterization of inorganic nutrients such as nitrogen (N) and phosphorus (P) is crucial because they directly affect fisheries output, the global carbon budget, and water quality (Taillardat, 2020). Red tide ecological disasters are more likely to occur when nutrients are abundant, water clarity is good, and the temperature is appropriate (ROSENBERG, 2008). After algae die, organic matter begins to decompose, depleting a significant amount of dissolved oxygen, which causes hypoxia in the bottom water. The relationship between nutrients and the triggering mechanism of red tide is tightly associated in terms of time, place, and scale (Wang et al. 2014, Ülkü et al. 2017).

Estuaries are complex environments characterized by spatial and temporal variation in physical, chemical and biological features. The complex processes occurring in estuaries alter the concentrations and fluxes in river runoff, impacting the ecological health of estuarine and coastal waters (Shulkin et al. 2018). Estuaries serve as key pathways connecting rivers and oceans, with over 87% of land being connected to the ocean through estuaries. Rivers transport terrestrial nutrients and dissolved organic carbon (DOC), which are principal pathways for the entry of DOC and other biogenic substances into the ocean (Bauer & Bianchi 2011). Estuary systems and human activities are closely intertwined as they provide people with access to the natural resources, energy and suitable living conditions. However, under the influence of human activities and climate change, the estuarine ecosystem becomes vulnerable to issues such as eutrophication, toxic algal blooms, hypoxia, and pH shifts (Glibert et al. 2022).

Numerous recent research studies have focused on the spatiotemporal distribution and alterations of nutrients in estuary waters. For instance, using the worldwide NEWS-DIP model, LI estimated phosphorus (P) inputs to the Yangtze River Basin and the exports of dissolved inorganic phosphorus (DIP) from the river to the estuary from 1970 to 2003 (Li et al. 2011). Nitrate nitrogen is the primary component of inorganic nitrogen in various estuarine water bodies (Reckhardt et al, 2015). The main sources of nutrients in estuarine water bodies include

river input, groundwater input, atmospheric sedimentation, and exchange with offshore water (Cho et al. 2018). Rivers are primarily responsible for transporting nutrients from land to estuaries and coastal areas (Sharples et al. 2017).

The intake of nitrogen (N), phosphorus (P), and silicon (Si) in estuaries and their nearshore waters is often imbalanced due to the substantial discrepancies between the main sources and influencing factors of these nutrients. This leads to substantial changes in their nutrient structure (Liu et al. 2019). The imbalance in the proportion of nutrient structure of estuaries is characterized by “more nitrogen, less phosphorus, and less silicon” (Zhang et al. 2007), which can result in shifts in dominant populations, a decline in biodiversity, an increase in toxic red tide algae, as well as other ecosystem variations (Song et al. 2017).

Human activities have a considerable impact on the water discharged from the Yangtze river outflow and along the bank of the Yangtze River estuary, resulting in the delivery of a large amount of nutrients into the estuary area (Liu et al. 2021). The water from the Yangtze River water has a dramatic effect on the physical and chemical properties of nutrients in the surrounding waters due to substantial changes in nutrient parameters once it enters the sea (Zhang et al. 2020). Some areas experience high levels of eutrophication. The concentrations of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) in the Yangtze River estuary have increased by 6.7 and 6 times, respectively, between 1960 and 2000 (Statham et al. 2012). According to Yang (2023), the flows of total phosphorus (TP) and total nitrogen (TN) are, on average, 8% lower than the previous five-year period (1999–2003), indicating a moderated increase in river nutrient flux over the past 20 years (2004–2020). Due to intensifying eutrophication and an unbalanced nutrient structure, red tides and other ecological catastrophes are prevalent in the Yangtze River estuary.

In order to comprehensively understand the level of eutrophication and identify the sources of dissolved nutrients, a systematic study was conducted in the spring and summer of 2019 in the Yangtze River estuary. The study focused on analyzing the concentration, horizontal distribution, and structural composition of nutrients. The findings from this study will contribute to advancing our knowledge of nutrient composition and eutrophication levels in the estuary, providing a rationale for implementing effective eutrophication control measures. This information is crucial for the conservation of coastal waters.

Material and methods

Two seasonal investigations were conducted in May and August of 2019. Seventeen observation stations were set up in the Yangtze River estuary (Figure 1). Water samples were collected from both the surface layer and the bottom layers at a depth of more than 10 m. On board the research vessel, the water samples were filtrated using fired Whatman GF/F filters (0.45 μm). The filtered samples were then preserved in polyethylene bottles containing 0.3% chloroform and stored under cryopreservation for subsequent laboratory analysis.

The concentrations of inorganic nutrients, including $\text{PO}_4^{3-}\text{-P}$, $\text{SiO}_3^{2-}\text{-Si}$, $\text{NO}_2^-\text{-N}$, $\text{NO}_3^-\text{-N}$, $\text{NH}_4^+\text{-N}$, were measured using an automatic analyzer (SKALAR, Netherlands). The

dissolved inorganic nitrogen (DIN) was calculated as the sum of $\text{NO}_2^-\text{-N} + \text{NO}_3^-\text{-N} + \text{NH}_4^+\text{-N}$. The chemical oxygen demand (COD) was determined using the alkaline potassium permanganate method. Salinity measurements of seawater were taken on site using a multiparameter analyzer (YSI, USA).

Data Processing

All statistical analyses were performed using SPSS 17.0 software. One Way Analysis of Variance (ANOVA) was conducted to assess the variations in nutrient concentrations across different seasons. Graphical presentations of nutrient concentrations against seasons were created for visual representation. Pearson's product-moment correlation matrix was used to identify the relationships among the nutrients and strengthen the results obtained from multivariate analysis. Additional charts can be generated using Sigma Plot 12.0 software.

Results

Seasonal Change of Nutrient

In spring, the mean concentrations of DIN (0.625 mg/L), $\text{SiO}_3^{2-}\text{-Si}$ (0.616 mg/L) and $\text{PO}_4^{3-}\text{-P}$ (0.031 mg/L) were measured at the surface layer of the sea area of the Yangtze River estuary. At the bottom layer, the values for DIN, $\text{SiO}_3^{2-}\text{-Si}$ and $\text{PO}_4^{3-}\text{-P}$ were 0.795 mg/L, 0.631 mg/L and 0.036 mg/L, respectively. In summer, the mean concentrations of DIN, $\text{SiO}_3^{2-}\text{-Si}$ and $\text{PO}_4^{3-}\text{-P}$ at the surface layer were 0.812 mg/L, 0.799 mg/L and 0.039 mg/L, respectively. For the bottom layer, the concentrations were 0.795 mg/L for DIN, 0.631 mg/L for $\text{SiO}_3^{2-}\text{-Si}$, and 0.036 mg/L for $\text{PO}_4^{3-}\text{-P}$ (Table 1).

Table 2 presents the correlation analysis between the nutrient and its salinity of the Yangtze River estuary in spring and summer. It shows that the concentration of DIN and $\text{SiO}_3^{2-}\text{-Si}$ showed a significant negative correlation with salinity ($n=40$, $P<0.01$) and the concentration of $\text{PO}_4^{3-}\text{-P}$ exhibited a weak correlation with salinity ($n=40$, $P>0.01$).

Stoichiometry and Trophic Structure of Nutrient and Mole Ration of Nutrient

The mole ratio of nutrients in the surface and bottom waters the Yangtze River estuary was measured during spring and summer (Table 3). The results showed that the mean specific values

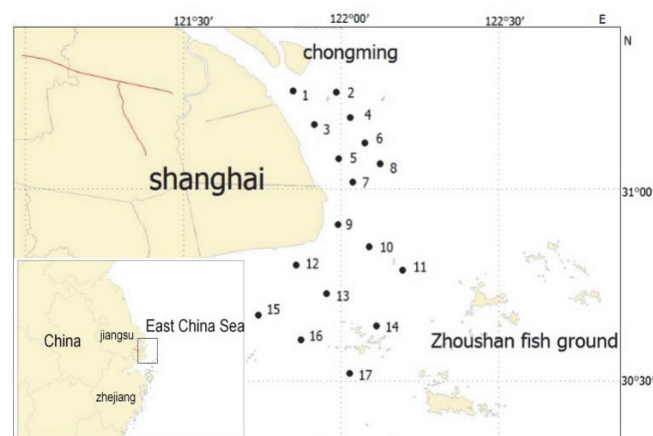


Fig. 1. Location of sampling stations

of $\text{SiO}_3^{2-}\text{-Si/PO}_4^{3-}\text{-P}$ at the surface and bottom layers were 36.528 ± 15.177 and 35.297 ± 10.278 , respectively. Similarly, the mean specific values of $\text{DIN/PO}_4^{3-}\text{-P}$ were 35.429 ± 11.820 and 35.641 ± 14.237 , respectively. The values of $\text{SiO}_3^{2-}\text{-Si/PO}_4^{3-}\text{-P}$, $\text{DIN/PO}_4^{3-}\text{-P}$ and $\text{SiO}_3^{2-}\text{-Si/DIN}$ were found to be significantly different between spring and summer. The mole ratios of these three nutrients in spring were lower than in summer.

According to the findings, significant regional differences were observed in the distribution of specific values of $\text{DIN/PO}_4^{3-}\text{-P}$, $\text{SiO}_3^{2-}\text{-Si/DIN}$, $\text{SiO}_3^{2-}\text{-Si/PO}_4^{3-}\text{-P}$, as evident from of dispersion point distributions (Figure 2). In spring, the ranges of specific values for $\text{DIN/PO}_4^{3-}\text{-P}$ $\text{SiO}_3^{2-}\text{-Si/PO}_4^{3-}\text{-P}$ in the surface layer were calculated as 19.801–31.493 and 9.258–33.692, respectively, while in the bottom layer they were 26.528–47.440 and 25.233–45.665, respectively. In summer, the ranges for the surface layers were 21.218–61.916 and 25.780–51.574, and for the bottom layers 26.434–57.360 and 29.363–54.229, respectively. The range of $\text{SiO}_3^{2-}\text{-Si/DIN}$

in the surface and bottom layers during spring was 0.839–1.299 and 0.840–1.173, respectively. In summer, the range was 0.708–1.645 for the surface layer, and 0.706–1.882 for the bottom layer.

Morphological Characteristics of DIN

Figure 3 showed that, in both spring and summer, $\text{NO}_3^- \text{-N}$ was the main form of DIN observed at the surface and bottom layers of the Yangtze River estuary. In spring, the relative amounts of inorganic nitrogen in the form of $\text{NO}_2^- \text{-N}$, $\text{NH}_4^+ \text{-N}$, and $\text{NO}_3^- \text{-N}$ at the surface layer were 0.028%, 0.227% and 0.745%, respectively. At the bottom layer, the relative amounts were 0.230%, 0.237% and 0.740%, respectively. As also, in summer for the surface the relative amount of $\text{NO}_2^- \text{-N}$, $\text{NH}_4^+ \text{-N}$, and $\text{NO}_3^- \text{-N}$ with 0.019%, 0.326%, and 0.655%, and the bottom layers of value was 0.019%, 0.354%, and 0.627%, respectively. The pattern of relative amounts of $\text{NH}_4^+ \text{-N}$ in spring and summer was opposite to that of $\text{NO}_2^- \text{-N}$ and $\text{NO}_3^- \text{-N}$.

Table 1. Statistical description of the nutrients concentrations in surface sediments and seawater from the Yangtze river estuary (mg/L)

| | DIN | | $\text{SiO}_3^{2-}\text{-Si}$ | | $\text{PO}_4^{3-}\text{-P}$ | |
|---------------|--------|--------|-------------------------------|--------|-----------------------------|--------|
| | spring | summer | spring | summer | spring | summer |
| Surface-Min | 0.359 | 0.332 | 0.359 | 0.390 | 0.014 | 0.005 |
| Surface-Max | 1.113 | 1.414 | 1.211 | 1.171 | 0.040 | 0.140 |
| Surface-Mean | 0.625 | 0.812 | 0.616 | 0.799 | 0.031 | 0.039 |
| Surface-SD | 0.205 | 0.221 | 0.227 | 0.224 | 0.008 | 0.036 |
| Surface-CV(%) | 32.80 | 27.22 | 36.85 | 28.04 | 25.81 | 92.31 |
| Bottom-Min | 0.328 | 0.482 | 0.328 | 0.342 | 0.004 | 0.004 |
| Bottom-Max | 1.090 | 1.126 | 1.208 | 1.352 | 0.050 | 0.103 |
| Bottom-Mean | 0.795 | 0.784 | 0.631 | 0.815 | 0.036 | 0.043 |
| Bottom-SD | 0.221 | 0.250 | 0.230 | 0.315 | 0.015 | 0.034 |
| Bottom-CV(%) | 27.80 | 31.89 | 36.45 | 38.65 | 41.67 | 79.07 |

Table 2. The correlation between nutrients and salinity in spring and summer in the Yangtze river estuary (samples n=40 respectively, significance level $\alpha=0.01$)

| nutrients at surface layer | DIN | $\text{SiO}_3^{2-}\text{-Si}$ | $\text{PO}_4^{3-}\text{-P}$ | Salinity | nutrients at bottom layer | DIN | $\text{SiO}_3^{2-}\text{-Si}$ | $\text{PO}_4^{3-}\text{-P}$ | Salinity |
|-------------------------------|---------|-------------------------------|-----------------------------|----------|-------------------------------|---------|-------------------------------|-----------------------------|----------|
| DIN | 1 | | | | DIN | 1 | | | |
| $\text{SiO}_3^{2-}\text{-Si}$ | 0.952* | 1 | | | $\text{SiO}_3^{2-}\text{-Si}$ | 0.701* | 1 | | |
| $\text{PO}_4^{3-}\text{-P}$ | 0.368 | 0.213 | 1 | | $\text{PO}_4^{3-}\text{-P}$ | 0.255 | 0.096 | 1 | |
| Salinity | -0.798* | -0.937* | -0.199 | 1 | Salinity | -0.823* | -0.814* | -0.296 | 1 |

“**” indicates the significant correlation above 0.01, and black words in bold indicate the correlation between the nutritive salt and salinity in summer.

Table 3. The mole ratios of nutrients in the surface and bottom waters in spring and summer of the Yangtze river estuary

| Item | Surface layer | | | Bottom layer | | |
|------------|--|-----------------------------------|---------------------------------|--|-----------------------------------|---------------------------------|
| | $\text{SiO}_3^{2-}\text{-Si/PO}_4^{3-}\text{-P}$ | $\text{SiO}_3^{2-}\text{-Si/DIN}$ | $\text{DIN/PO}_4^{3-}\text{-P}$ | $\text{SiO}_3^{2-}\text{-Si/PO}_4^{3-}\text{-P}$ | $\text{SiO}_3^{2-}\text{-Si/DIN}$ | $\text{DIN/PO}_4^{3-}\text{-P}$ |
| Spring | 24.434±9.258 | 0.945±0.126 | 25.647±5.846 | 35.449±10.216 | 0.987±0.109 | 36.984±10.456 |
| Summer | 41.897±15.463 | 1.123±0.346 | 41.567±20.349 | 41.796±12.433 | 1.198±0.221 | 38.677±12.897 |
| Mean value | 36.528±15.177 | 1.003±0.198 | 35.429±11.820 | 35.297±10.278 | 1.123±0.346 | 35.641±14.237 |

Evaluation of Eutrophication

This article evaluates the eutrophication in the sea area of Yangtze River estuary by adopting the Eutrophication Index (E) method (LIU 2011) as given below:

$$E = \text{COD} \times \text{DIN} \times \text{DIP} \times 10^6 / 4500 \quad (1)$$

In the formula, the concentrations of COD, DIN, and DIP are all in mg/L.

By substituting the test data of COD, DIN, and DIP from each investigation site in the Yangtze River estuary

in Formula (1), the ranges of Eutrophication Index (*E*) for each investigation site in spring and summer were calculated as 0.915–18.324 and 0.854–53.29, respectively. The Eutrophication Index (*E*) values in spring were much lower than those in summer (Table 4).

Discussion

Seasonal Change

In spring, the concentrations of nutrients at surface and bottom layers were notably lower than those in summer, which can

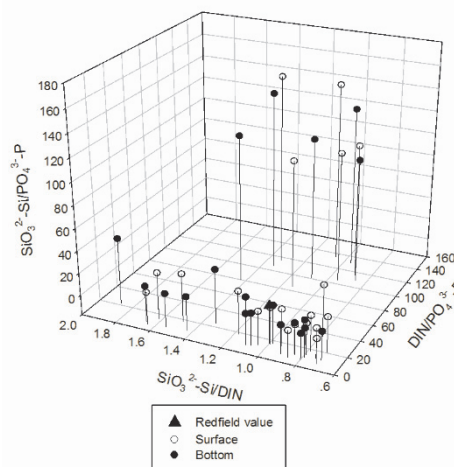
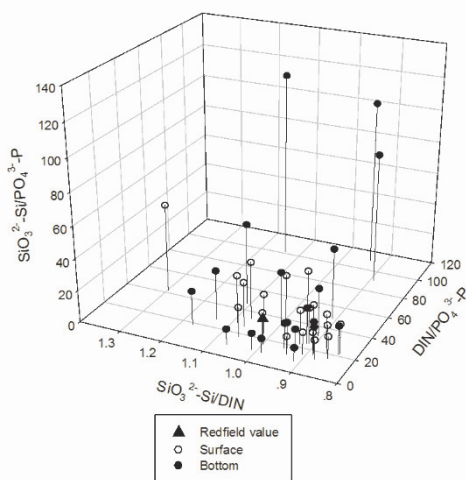


Fig. 2. The scatter distribution of $\text{DIN}/\text{PO}_4^{3-}\text{-P}$, $\text{SiO}_3^{2-}\text{-Si}/\text{DIN}$, $\text{SiO}_3^{2-}\text{-Si}/\text{PO}_4^{3-}\text{-P}$ in spring (a) and summer (b) in the Yangtze river estuary

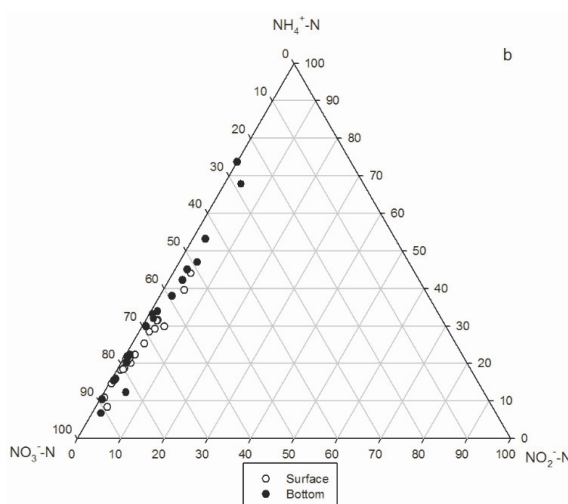
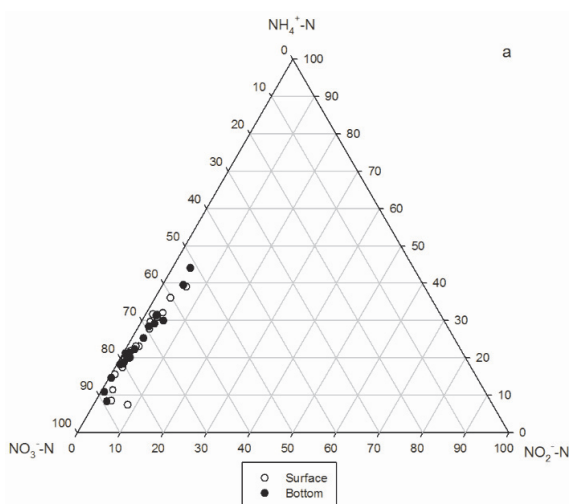


Fig. 3. The relative content of $\text{NO}_2^- \text{-N}$, $\text{NO}_3^- \text{-N}$, $\text{NH}_4^+ \text{-N}$ in spring (a) and summer (b) of the Yangtze river estuary

Table 4. The trophic state index (*E*) of nutrients in waters and spring and summer in the Yangtze river estuary

| Item | Spring | | Summer | |
|------|-----------|--------|-----------|--------|
| | COD(mg/L) | E | COD(mg/L) | E |
| Min | 0.12 | 0.915 | 0.09 | 0.854 |
| Max | 3.17 | 18.324 | 3.19 | 53.29 |
| Mean | 0.73 | 5.896 | 0.68 | 23.753 |

be attributed to the influence of phytoplankton and the runoff from the Yangtze river (LU 2023). Numerous studies on nutrient absorption kinetics have indicated threshold values for the growth of phytoplankton, which are 0.014 mg/L for DIN, 0.056 mg/L for $\text{SiO}_3^{2-}\text{-Si}$, and 0.003 mg/L for $\text{PO}_4^{3-}\text{-P}$ (BROWN 1979, SHEN et al. 2011, NELSON 1990). The mean concentrations of each nutrient in the sea areas of the Yangtze River estuary were higher than the threshold values. In spring, as phytoplankton undergo vigorous growth, the upper layer of the water column absorbs a significant amount of nutrients, leading to a sharp reduction in DIN, $\text{SiO}_3^{2-}\text{-Si}$ and $\text{PO}_4^{3-}\text{-P}$ concentrations (Shen et al. 2011). Conversely, the organisms in the lower layer release nutrients through reproduction (Ząbek_2013). In summer, during the flood season of rivers like the Yangtze river, the concentrations of DIN, $\text{SiO}_3^{2-}\text{-Si}$ and $\text{PO}_4^{3-}\text{-P}$ are much higher than in spring due to increased runoff from the land into the ocean.

In general, nutrient concentrations in many diverse areas exhibit high values and show spatial heterogeneity due to the complex interplay of physical, chemical, and biological processes. In natural marine environments, nutrient inputs mainly come from three sources: vertical mixing, horizontal transportation, and atmospheric deposition (HUSNAIN 2009, Sarma 2023). Evaluating the addition, transfer, and preservation of nutrients can be achieved by examining their correlation with salinity (Melissa 2013). According to the findings, a significant negative correlation was observed between salinity and both DIN and $\text{SiO}_3^{2-}\text{-Si}$ in the study area. This indicates that the concentration of DIN and $\text{SiO}_3^{2-}\text{-Si}$ is influenced by the runoff inputs from the main rivers of the Yangtze river, as well as the physical mixing process, and temporal fluctuations. The strong scouring action caused by the influx of runoffs from the land leads to a higher migration speed of DIN and $\text{SiO}_3^{2-}\text{-Si}$ compared to the utilization speed by organisms, resulting in the conservative behavior of DIN and $\text{SiO}_3^{2-}\text{-Si}$ concentrations.

Furthermore, there was no significant correlation between salinity and $\text{PO}_4^{3-}\text{-P}$, indicating different main sources for $\text{PO}_4^{3-}\text{-P}$ and DIN in the sea area. The concentration of DIN is primarily influenced by several processes, such as the diluted water from the Yangtze river, biological activity, and the input of high-salinity seawater (Zheng et al. 2020). The spatial distribution of $\text{PO}_4^{3-}\text{-P}$ is closely related to the buffering mechanism at the estuary and the release of nutrients by the interfaces of bottom sediments (Biswas 2011). The buffering mechanism of $\text{PO}_4^{3-}\text{-P}$ is largely controlled by the interaction between particulate matter and water at the estuary (Sun et al. 2019). Suspended solids, with their strong adsorptive capacity, absorb a high amount of $\text{PO}_4^{3-}\text{-P}$ from waters with high particulate matter content, while $\text{PO}_4^{3-}\text{-P}$ from waters with low particulate matter content. As a result, the concentration of $\text{PO}_4^{3-}\text{-P}$ exhibits minimal variation throughout the estuary (Chen et al. 2010).

Structure of Nutrient

The mole ratios of $\text{DIN}/\text{PO}_4^{3-}\text{-P}$, $\text{SiO}_3^{2-}\text{-Si}/\text{DIN}$, $\text{SiO}_3^{2-}\text{-Si}/\text{PO}_4^{3-}\text{-P}$ can reflect the nutrient status in the seawater. The mole ratio of the nutrient is made according to requirement nutrient of diatom (LI et al. 2017). In general, the atomic ratio of $\text{SiO}_3^{2-}\text{-Si}:\text{DIN}:\text{PO}_4^{3-}\text{-P}$ is 16:16:1, and this

ratio value changes owing to physical, biological, and chemical factors in different sea areas. Appropriate specific values of $\text{DIN}/\text{PO}_4^{3-}\text{-P}$, $\text{SiO}_3^{2-}\text{-Si}/\text{DIN}$, and $\text{SiO}_3^{2-}\text{-Si}/\text{PO}_4^{3-}\text{-P}$ are beneficial to the growth and reproduction of phytoplankton. Conversely, the lack of nutrients limits phytoplankton growth and reproduction. Excessively high concentrations and imbalanced distribution of nutrients also highly influence the population structure of plankton, even causing red tide (Redfield, 1963). In estuaries, the ratios of nutrient and several physical conditions may be more important for eutrophication regulation and control than the concentration of a single nutrient (Vinita et al. 2015). The change in values of $\text{DIN}/\text{PO}_4^{3-}\text{-P}$, $\text{SiO}_3^{2-}\text{-Si}/\text{DIN}$, $\text{SiO}_3^{2-}\text{-Si}/\text{PO}_4^{3-}\text{-P}$ reflects nutrient input from the land, ocean current, atmospheric sedimentation, and human activities' influence, as well as nutrient regeneration and cycling mechanisms in seawater.

We found that the mole ratio of $\text{SiO}_3^{2-}\text{-Si}/\text{PO}_4^{3-}\text{-P}$ and $\text{DIN}/\text{PO}_4^{3-}\text{-P}$ were both higher than the Redfield value, while the values of $\text{SiO}_3^{2-}\text{-Si}/\text{DIN}$ were closer to Redfield value (Redfield, 1963). This indicates an unbalanced proportion of nutrients in the water area of the Yangtze River estuary. Differences in molar ratios of nutrients in spring and summer have fully demonstrated the influence of limiting phytoplankton growth and reproduction (JULIA, 2012). The results showed that $\text{PO}_4^{3-}\text{-P}$ was the potential limiting factor of phytoplankton in the water area of Yangtze River estuary, whereas DIN and $\text{SiO}_3^{2-}\text{-Si}$ were not limiting factors for diatom. The nutrient structure and limitations on nutrition in different regions are remarkably different, influenced by various factors such as illumination and water temperature (Liu et al. 2019).

Moreover, the construction of large reservoirs will also intercept the nutrient flux into the sea. Human-built dams indirectly regulate the input of DIP, DSi by altering the hydrological conditions of river waters (Chen et al. 2014). The construction of dams and reservoirs may intercept some DSi or change P form (from DIP to DOP), reducing nutrient transportation downstream (Szatten, 2021) and affecting the coastal marine environment (CHRISTOPH et al. 2000). According to statistics, dams have reduced P, and Si output fluxes of global rivers by 43%, and 21%, respectively (Maavara et al. 2017). The values of $\text{DIN}/\text{PO}_4^{3-}\text{-P}$, $\text{SiO}_3^{2-}\text{-Si}/\text{DIN}$ may be related to the significant dam construction that can reduce both silica and phosphorus exports through the Yangtze River.

Morphological Characteristics of DIN

DIN includes three forms: $\text{NO}_2^-\text{-N}$, $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in seawater. DIN plays a vital role in the circulation of living food in the marine environment. When ammonization and nitrification are fully carried out, nitrogen in various forms reaches a thermodynamic equilibrium (Avik 2013). The Yangtze River estuary, being an open sea area with good water exchange conditions, has achieved a thermodynamic equilibrium for DIN. The relative amounts of $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$ show opposite trends from spring to summer. The relative amount $\text{NH}_4^+\text{-N}$ increases as the metabolism of creatures becomes more prosperous, leading to increased discharge. Additionally, the variation in nutrient concentration is closely related to high water temperature in summer (which accelerates organic matter oxygenolysis) and bacterial activity,

which accelerates the degradation of organic matter and releases more $\text{NH}_4^+\text{-N}$ (Zhao et al. 2019).

Eutrophication level

Eutrophication Index (E) ≥ 1 indicates that eutrophication has occurred in waters. Higher values of E indicate a more serious degree of eutrophication (Liu 2011). The mean values of E for two seasons in the Yangtze River estuary were much higher than the threshold, indicating a serious degree of eutrophication in the Yangtze River estuary. Therefore, significant attention and urgent action are necessary. However, although, the Yangtze River estuary exhibited a severe eutrophication level, nutrient concentrations were lower compared to anthropogenically disturbed estuaries like the Razdolnaya river (Shulkin et al. 2018), the Pasur river estuary (Hasan et al. 2020), Kanyakumari (Rathika, 2018) and Itchen estuary (Shi, 2019) in other countries, including Bohai Bay (Liu et al. 2019) and the Yellow river estuary (Luo et al. 2020) in China (Table 5). The nutrient conditions of estuaries and bays in different regions can vary due to many environmental impact factors such as the unique circulation, complex topography, vertical gradient, and different dynamic characteristics of the river-sea boundary (Coffin et al. 2021).

Conclusion

In spring and summer, the concentrations of DIN and $\text{SiO}_3^{2-}\text{-Si}$ at the surface and bottom layers were mainly limited by the input of runoffs from main rivers such as the Yangtze river, and the physical mixing process with the external ocean current of the Yangtze River estuary. $\text{PO}_4^{3-}\text{-P}$ showed a buffer mechanism and its distribution was relatively complicated at the Yangtze River estuary. The concentration of each nutrient had distinct feature of seasonal variation.

The Yangtze River estuary displayed an unbalanced proportion of nutrients. The specific value of $\text{SiO}_3^{2-}\text{-Si}/\text{PO}_4^{3-}\text{-P}$ and $\text{DIN}/\text{PO}_4^{3-}\text{-P}$ at the surface and bottom layers in spring and summer surpassed the Redfield values. $\text{PO}_4^{3-}\text{-P}$ was the potential limiting factor in the Yangtze River estuary during these seasons. The distributions of specific values of $\text{DIN}/\text{PO}_4^{3-}\text{-P}$, $\text{SiO}_3^{2-}\text{-Si}/\text{DIN}$, and $\text{SiO}_3^{2-}\text{-Si}/\text{PO}_4^{3-}\text{-P}$ were inconsistent in the sea area.

In spring and summer, $\text{NO}_3^-\text{-N}$ was typically the major form of DIN at the surface and bottom layers in the sea area of Yangtze River estuary, and DIN had fully reached thermodynamic equilibrium. In these two seasons, the Eutrophication Index (E) exceeded the eutrophication threshold value, indicating a severe eutrophication.

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Table 5. Comparison of nutrient levels between Yangtze river estuary and other estuary(mg/L)

| Location | Year | DIN | $\text{SiO}_3^{2-}\text{-Si}$ | $\text{PO}_4^{3-}\text{-P}$ | reference |
|--------------------------|-----------|------|-------------------------------|-----------------------------|----------------------|
| Razdolnaya river estuary | 2014–2015 | 1.58 | 15.6 | 0.12 | Shulkin et al., 2018 |
| Kanyakumari estuary | 2011–012 | 4.67 | - | 1.26 | Rathika, 2018 |
| Itchen estuary | 2009 | – | 5 | 0.10 | Shi, 2019 |
| Pasur river estuary | 2019 | 1.10 | 1.38 | 1.53 | Hasan et al., 2022 |
| Bohai bay | 2013-2014 | 1.39 | 0.28 | 0.06 | Liu et al., 2019 |
| Yellow river estuary | 2004-2019 | 0.46 | 0.97 | 0.08 | Luo et al., 2022 |
| Yangtze river estuary | 2019 | 0.75 | 0.72 | 0.04 | This study |

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