

Characteristics of Nutrients and Eutrophication Assessment of Shenzhen Offshore Waters

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Abstract. Based on the data obtained in the coastal waters of Shenzhen from the Guangdong Environmental Monitoring Center, the distribution of DIN, DIP were analyzed, and the temporal spatial variations of nutrient level and organic pollution situation were evaluated using methods such as single factor index, eutrophication index, and water organic pollution evaluation index. The results show that the nutrient level of the eastern waters was lower than that of the western. The Dapeng Bay and Daya Bay comply with the first-class seawater standard, the Zhujiang Estuary and Shenzhen Bay exceed the fourth-class seawater standard. And there were some similarities between the eutrophication and organic pollution spatial distribution, and the eutrophication and organic pollution were observed in the western waters. The correlation analysis suggested there was a negatively correlation between salinity and major pollutants ($P < 0.01$), implying the relationship between terrigenous pollution and the content of environmental elements.

1. Introduction

Shenzhen is located on the coast of the South China Sea, with its sea area spreading 1145 square kilometers and a coastline 257.3km. Separated by the Kowloon Peninsula, the sea area is divided into two parts, the Eastern and Western. The eastern part includes Dapeng Bay and Daya Bay, the western part includes Shenzhen Bay and Zhujiang Estuary. Shenzhen is rich in marine biological resources and fishery resources. Tourism and port resources are developed. However, with the rapid development of the economy, large amounts of pollutants discharged into the sea, resulting in the decreased quality of seawater environment, increased eutrophication level ^[1], and high occurrence frequency of HABs. According to historical records ^[2] and surveys, during the period from 1981 to 2014, a total of 162 occurrences of HABs were recorded. The phenomenon of frequent occurrence of HABs has been highly concerned by governments and scientists around the world ^[3,4]. The mechanism of HABs occurrence was very complicated, involving meteorological, hydrological, biological, chemical and other aspects. Most studies suggest that the occurrence of HABs was closely related to the eutrophication ^[5]. Dissolved inorganic nitrogen (DIN) and phosphate (DIP) were the basic nutrients for phytoplankton growth ^[6]. Based on the monitoring data of the spring and autumn seasons in Shenzhen's coastal waters in 2015, this paper analyzes the level of eutrophication and organic pollution, and discusses the correlation



between the main environmental parameters. This study will provide a basic support for the development and utilization of marine resources and environmental protection in Shenzhen coastal area.

2. Environmental elements and research methods

2.1. Environmental elements

Datas obtained in the coastal waters of the Shenzhen from the Guangdong Environmental Monitoring Center, that included water temperature(T), salinity(SAL), dissolved oxygen(DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD), dissolved inorganic nitrogen(DIN), phosphate (DIP), etc..

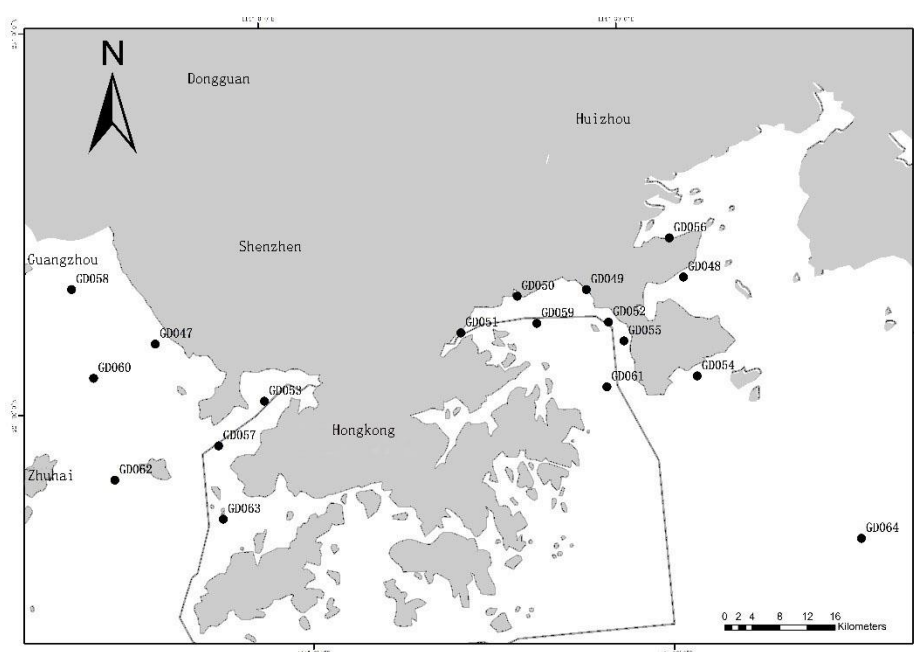


Fig 1. Sampling stations of Shenzhen offshore Waters

2.2. Research methods

2.2.1. Single factor index.

The single factor index method was used to evaluate the environmental quality of sea areas [7]. The formula is as follows.

$$P_i = C_i / C_{si}$$

In the formula, P_i is the pollution index, C_i is the actual concentration, C_{si} is the evaluation criterion. If the pollution index $P_i > 1.0$, which means "Pollution is observed". The evaluation adopts the first-class standard of "Sea Water Quality Standard" (GB3097-1997) [8,9].

2.2.2. Eutrophication index.

The eutrophication evaluation uses eutrophication index [10]. The formula is as follows.

$$E_i = COD \times DIP \times DIN \times 10^6 / 4500$$

In the Formula, E is the eutrophication index, COD is the chemical oxygen demand, DIN is the dissolved inorganic nitrogen, DIP is the phosphate.

The eutrophication index is divided into five grades, as shown in the table 1.

Table 1. Classification standard of water eutrophication evaluation

E	Trophic level	Nutritinal status
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0~0.5	1	Poor nutrition
0.5~1.0	2	Nutrition
1.0~3.0	3	Mild Eutrophication
3.0~9.0	4	Moderate Eutrophication
>9.0	5	Severe Eutrophication

2.2.3. Organic pollution index.

The organic pollution index uses *COD*, *DIN*, *DIP* and *DO* to evaluate seawater quality and reflects the overall condition of water quality [11]. The formula is as follows.

$$A_i = \frac{COD}{COD_s} + \frac{DIP}{DIP_s} + \frac{DIN}{DIN_s} - \frac{DO}{DO_s}$$

In the Formula, *COD* is the chemical oxygen demand, *DIN* is the dissolved inorganic nitrogen, *DIP* is the phosphate, *DO* is the dissolved oxygen. And *COD_s*, *DIN_s*, *DIP_s*, *DO_s* are evaluation criteria for the above indicators, which adopt the first-class standard of "Sea Water Quality Standard" (GB3097-1997).

The organic pollution index is divided into six grades, as shown in the table 2.

Table 2. Classification standard of organic pollution evaluation

A	Organic pollution level	Water quality
<0	0	Favorable
0~1.0	1	Not polluted
1.0~2.0	2	Begin to be polluted
2.0~3.0	3	Mildly Polluted
3.0~4.0	4	Moderately Polluted
>4.0	5	Severely Polluted

3. Evaluation results and analysis

3.1. The characteristic of DIN distribution

By studying the composition of DIN, in spring, the percentages of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and $\text{NO}_2^-\text{-N}$ in surface seawater are 33.1%, 45.8% and 27.2%, respectively. In autumn, the percentages are 20.7%, 36.5% and 42.8%, respectively. Thus, DIN is mainly dominated by the presence of $\text{NO}_3^-\text{-N}$, and $\text{NO}_2^-\text{-N}$.

The DIN concentration in the eastern waters is much lower than that of western waters. Judging from the annual single factor index of the DIN, the eastern seawater quality complies with the first-class seawater standard, the western seawater quality exceeds the fourth-class seawater standard, the single factor indexes of Dapeng Bay, Daya Bay, Zhujiang Estuary and Shenzhen Bay are 0.6, 0.5, 5.1 and 4.8, respectively. In spring, the single factor indexes of Dapeng Bay and Daya Bay are 0.2 and 0.1, respectively. In autumn, the single factor indexes of Dapeng Bay and Daya Bay are both 0.9. In spring, the single factor indexes of the Zhujiang estuary and Shenzhen Bay are 7.2 and 6.4, respectively. In autumn, that are 3.0 and 3.1, respectively. Judging from the evaluation results, the quality of Zhujiang Estuary and Shenzhen Bay were worse in spring than that in autumn, while Dapeng Bay and Daya Bay's results are exactly the opposite.

Table 3. Results of DIN、DIP Single Factor Index

Area	Zhujiang Estuary			Shenzhen Bay			Dapeng Bay			Daya Bay		
Season	SP	AU	AV	SP	AU	AV	SP	AU	AV	SP	AU	AV
DIN	7.2	3	5.1	6.4	3.1	4.8	0.2	0.9	0.6	0.1	0.9	0.5

DIP	1.3	3.2	2.3	2.4	5.5	4.0	0.1	0.8	0.5	0.2	0.7	0.5
SPR=Spring, AUT=autumn, AVG=Average												

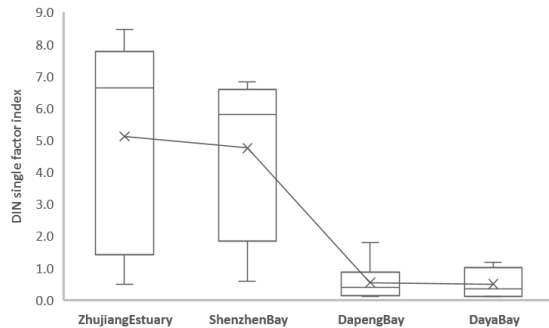


Figure 2. Annual results of DIN single factor index

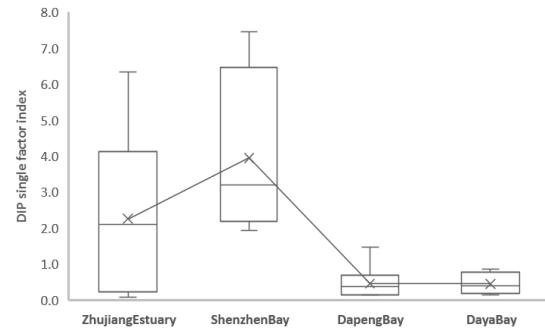


Figure 3. Annual results of DIP single factor index

3.2. The characteristic of DIP distribution

The distribution of DIP single factor index is generally similar to the DIN. The water quality of the eastern sea area is better than that of the western. Judging from the annual single factor index of the DIP, the eastern seawater quality comply with the first-class seawater standard, the Zhujiang Estuary quality comply with the third-class seawater standard, the water quality of Shenzhen Bay is inferior to the Zhujiang Estuary. The single factor indexes of Dapeng Bay, Daya Bay, Zhujiang Estuary and Shenzhen Bay are 0.5, 0.5, 2.3 and 4.0, respectively. In spring, the single factor indexes of Dapeng Bay and Daya Bay are 0.1 and 0.2, respectively. In autumn, the single factor indexes of Dapeng Bay and Daya Bay are 0.8 and 0.7, respectively. The Shenzhen Estuary's indexes are 2.4 in spring and 5.5 in autumn, spring water quality can comply with fourth-class seawater standard, autumn water quality is inferior to that of spring. The Zhujiang Estuary's indexes are 1.3 in spring and 3.2 in autumn, Spring water quality comply with fourth-class seawater standard, and autumn water quality is inferior to that of spring. The eastern sea area and the western sea area all show the same pattern, that is, the spring results are better than the autumn ones.

3.3. The characteristic of Eutrophication index(E) distribution

According to calculations, the E value in the eastern sea area is much lower than that in the western sea area. The E value range of the eastern sea area ranges from 0.01 to 3.85, with an average value of 0.35, which is considered as "poor nutrition". The points with $E < 0.5$ account for 88.9%. The E value range of the western sea ranges from 0.6 to 31.7, with an average value of 12.0, which is considered as "severe eutrophication". The points with $E > 9$ accounts for 50%. Judging from different seasons, the maximum value of E in Dapeng Bay and Daya Bay in the eastern sea area in spring is 0.03, which is considered as "poor nutrition". The E value of Dapeng Bay in autumn is 0.82, which is considered as "Nutrition". The E value of Daya Bay is 0.20, which is considered as "poor nutrition". The points where the E value is less than 0.5 in the eastern part of the autumn account for more than 80%. The E value of the Zhujiang Estuary in the western waters is 7.2, which is considered as "moderate eutrophication". With an E value of 21.1, the Shenzhen Bay is considered as "Severe eutrophication", and 83.3% of the points' E value in the western are higher than 3 in spring; The E values of the Zhujiang Estuary and Shenzhen Bay in the autumn are 12.0 and 12.4, respectively, and they are both considered as "severe eutrophication".

Table 4. E value and evaluation of sea water quality

Area	Seasons	E		
		Range	Average	Evaluation
Zhujiang Estuary	Spring	1.0~21.1	7.2	Moderate Eutrophication
	Autumn	0.6~29.3	12.0	Severe Eutrophication

Shenzhen Bay	Spring	10.5~31.7	21.1	Severe Eutrophication
	Autumn	7.0~17.8	12.4	Severe Eutrophication
Dapeng Bay	Spring	0.01~0.03	0.01	Poor nutrition
	Autumn	0.05~3.85	0.82	Nutrition
Daya Bay	Spring	0.01~0.03	0.02	Poor nutrition
	Autumn	0.07~0.32	0.20	Poor nutrition

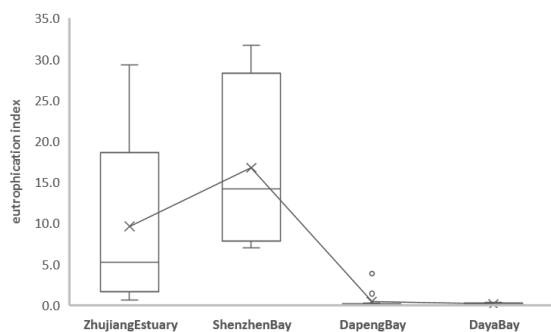


Figure 4. Annual results of eutrophication index

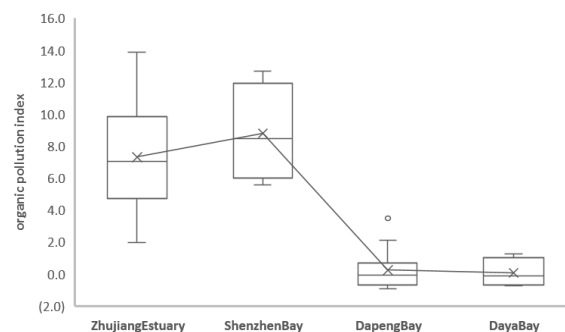


Figure 5. Annual results of organic pollution index

3.4. The characteristic of Organic pollution index(A) distribution

According to calculations, The A value in the eastern sea area is far lower than that in the western sea area, and the organic pollution in the western sea area of the Shenzhen Bay is relatively serious. Annually, the A value range of the eastern sea area range from -0.9 to 3.5, with an average value of 0.2 which is considered as "not polluted", and the points with $A < 1.0$ account for 83.3%. The A value range of the western sea area range from 1.9 to 13.9, with an average value of 12.0 which is considered as "severe pollution", and the points with $A > 9$ account for 90%. In spring, the A value range of Dapeng Bay range from -0.9 to 0.3, with an average value of 0.6 which is considered as "not polluted". In autumn, the A value range of Dapeng Bay range from 0.07 to 3.5, with an average value of 1.11 which is considered as "began to be polluted". In spring, the A value range of Daya Bay range from -0.7 to 0.5, with an average value of -0.6. And in autumn, the A value range of Daya Bay range from 0.3 to 1.3, with an average value of 0.8. Both are considered as "not polluted". In spring, the A value range of Zhujiang estuary range from 6.9 to 10.3, with an average of 8.2 which is considered as "severe pollution". The A value range of Zhujiang estuary ranges from 1.9 to 13.9, in autumn, with an average of 6.4 which is considered as "severely polluted." The A values of the Shenzhen Bay are 8.5 in spring and 9.1 in autumn, which are considered as "severely polluted".

Table 5. A value and evaluation of sea water quality

Area	Seasons	A		
		Range	Average	Evaluation
Zhujiang Estuary	Spring	6.9~10.3	8.2	Severely Polluted
	Autumn	1.9~13.9	6.4	Severely Polluted
Shenzhen Bay	Spring	7.4~9.6	8.5	Severely Polluted
	Autumn	5.6~12.7	9.1	Severely Polluted
Dapeng Bay	Spring	-0.9~-0.3	-0.6	Not polluted
	Autumn	0.07~3.5	1.11	Begin to be polluted
Daya Bay	Spring	-0.7~-0.5	-0.6	Favorable
	Autumn	0.3~1.3	0.8	Not polluted

3.5. Correlation analysis

SPSS 19.0 is used to analyze the correlation of environmental elements. The results show that temperature is a key factor in controlling the change of seawater environment. DO is mainly controlled by temperature. Generally, DO is mainly derived from sea-air exchange. The increase of temperature lowers the saturation of DO. The degree of DO concentration in the summer is generally low. ^[12]

The salinity is negatively correlated with major pollutants (COD, BOD and DIN), reflecting the impact of terrestrial input on the distribution of pollutants in the offshore region. However, there is no obvious correlation between SAL and DIP, indicating that DIP is less affected by runoff. Therefore, runoff contributes much to NO_3^- -N and NO_2^- -N, but does not contribute significantly to DIP ^[13,14].

DIN is positively correlated with NH_4^+ -N, NO_3^- -N and NO_2^- -N, especially with NO_3^- -N and NO_2^- -N, indicating that the DIN concentration distribution is mainly synchronized with NO_3^- -N and NO_2^- -N. Consistent with the analysis results of the aforementioned DIN composition.

Table 6. Correlations of environmental parameters in the coastal of Shenzhen

Factor	T	SAL	DO	COD	BOD	DIN	DIP	NH_4^+ -N	NO_3^- -N	NO_2^- -N
T	1.00									
SAL	-0.15	1.00								
DO	-0.25*	-0.15	1.00							
COD	0.09	-0.49**	0.20	1.00						
BOD	-0.07	-0.39**	0.45**	0.64**	1.00					
DIN	0.07	-0.36**	-0.17	0.22	0.11	1.00				
DIP	0.32**	-0.22	-0.40**	0.08	-0.17	0.34**	1.00			
NH_4^+ -N	-0.18	0.11	0.10	-0.09	0.02	0.39**	-0.10	1.00		
NO_3^- -N	-0.01	-0.56**	0.09	0.45**	0.32**	0.65**	0.30*	0.12	1.00	
NO_2^- -N	0.12	-0.27*	-0.24*	0.18	0.06	0.80**	0.39**	0.31*	0.49**	1.00

**represents $P < 0.01$, *represents $P < 0.05$, $n = 36$.

3.6. Results analysis

Based on the above analysis of the distribution characteristics of DIN, DIP, eutrophication index, and Organic pollution index, it is shown that the water quality in the western part of Shenzhen is relatively worse. The reasons for this phenomenon are, first of all, limited by natural conditions. The main reason for the poor water quality in the western is that the Shenzhen Bay water flow belongs to the semi-enclosed catchment tide bay, and the water exchange capacity is weak^[15]. The rivers around Dapeng Bay and Daya Bay in the eastern are short and contribute little surface runoff^[16]. Followed by the input of terrigenous pollution. In the western waters, there are the Shenzhen River and the Pearl River runoff, etc. The Shenzhen River mainly flows through Luohu District and Futian District and undertakes a large amount of industrial wastewater and domestic sewage. This is the main reason for the serious pollution of DIN and DIP in Shenzhen Bay. And this part of the sea area is also affected by the northwestern region of Hong Kong, and as an important sea transport channel, a variety of human activities cause increased pollution of nitrogen and phosphorus nutrients in the western waters. ^[9]

There is Daya Bay Aquatic Resources Nature Reserve in the eastern sea area, which is an important tourist coastline in Shenzhen. It has most of the coastal scenery and holiday resorts in Shenzhen, and there are fewer industrial enterprises. Therefore, there is less terrigenous pollution in the eastern sea area. It can be seen that terrigenous pollution is the main cause of pollution in Shenzhen's coastal waters.

4. Conclusion

The results show that the concentration level of the nitrogen and phosphorus nutrients in the eastern waters was lower than that of the western. The Dapeng Bay and Daya Bay in the eastern comply with the first-class seawater standard; the Zhujiang Estuary and Shenzhen Bay in the western exceed the fourth-class seawater standard. From the evaluation results in spring and autumn, the DIN results in

spring of the western sea area are inferior to those in autumn, while those in the eastern sea area are the opposite. The DIP results in spring are superior to autumn, both in the eastern and the western.

According to the evaluation results of eutrophication index, the degree of eutrophication in the eastern waters is relatively low, and the eutrophication pollution is not observed. Only several individual points in Dapeng Bay have reached the status of "nutrition". The Zhujiang Estuary and Shenzhen Bay in the western waters are both eutrophic, and Shenzhen Bay is relatively more eutrophic than the Zhujiang Estuary. Judging from the seasonal distribution, the degree of eutrophication in autumn is higher than that in spring. The evaluation results of the organic pollution index have similar distribution with the nutrient and eutrophication index. The extent of organic pollution in the eastern waters is relatively low, and it is in a "not polluted" state. Only in the fall of Dapeng Bay, it is "begin to be polluted". Western seawater are considered "severely polluted."

According to the negative correlation between SAL and major elements (COD, BOD₅, DIN), and the temporal and spatial variation of the marine environment elements in surveyed sea areas, the results indicate terrigenous pollution is the main reason for seawater quality of Shenzhen's offshore waters.

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