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Original Research

Spatio-Temporal Patterns and the Fluxes of Regional Nutrient Pollution in the Pearl River Basin, China

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Abstract

Anthropogenic activities have had a great impact on the characteristics of watershed pollution. The Pearl River basin is the third largest river in China, but it has been affected by eutrophication impact for a long time. This study comprehensively evaluated the nutrient pollution characteristics of the Pearl River basin from 2016 to 2018. The result shows that the ratio of total nitrogen (TN) and total phosphorus (TP), TN/TP was 24.7 of the Pearl River basin, which indicated that phosphorus was the restrictive factor for eutrophication problems. The limitation of TP maybe caused that TN is difficult to decrease through denitrification and nitrification. The fluxes of TN and TP remained stable in recent 20 years, and the flux of TN and TP transferred from the Pearl River basin to the ocean was 6.86×10^5 and 2.84×10^4 t in 2017, respectively. The Pearl River estuary had the largest discharge, accounting for more than 40% of the Pearl River basin. The TN in the West River and North River had a high pollution load, while TP pollution in the East River was very serious. It is necessary to establish an effective mechanism to control nitrogen and phosphorus. A large amount of nitrogen and phosphorus caused the decrease of dissolved oxygen (DO) and the increase of chemical oxygen demand (COD), which aggravated eutrophication. This study of nutrient elements fluxes and distribution in the Pearl River Basin are one of the important prerequisites for clarifying the causes of eutrophication, providing data and theoretical support for further water pollution control and water environmental protection in the future, and also providing a basis for pollution control decisions.

Keywords: nitrogen, phosphorus, flux, eutrophication, Pearl River

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Introduction

Seasonal eutrophication is an acute problem in all major rivers worldwide due to excessive nutrients in the surface water [1-3]. Nitrogen and phosphorus, as essential elements for biological activities, can cause algae blooming under suitable conditions, resulting in the adverse effects of the deteriorating water environment of eutrophication [3, 4]. In China, eutrophic elements in some major rivers have exceeded the environmental capacity for a long time, such as the Yangtze River and Pearl River, which posed a threat to water resources allocation, security, and sustainable development [5-7]. In addition, algae blooming such as red tides and green tides often occurred at the estuary, due to a large amount of nitrogen and phosphorus pollution accumulated. For example, since 2007, the green tide of *Ulva prolifera* disasters have consecutively occurred in the Yellow Sea at the turn of spring and summer for 15 years, which has severely affected the coastal marine ecosystem, caused huge economic losses, and affected sustainable development [8, 9]. Therefore, the nitrogen and phosphorus emission fluxes of major rivers need to be concerned to ensure river water quality and water resources allocation, as well as estuary ecological safety.

The problems of eutrophication are influenced by the concentration of the total nitrogen (TN) and total phosphorus (TP), the TN/TP ratio, temperature, and other environmental factors. For watershed pollution emissions, the fluxes of TN and TP and the TN/TP ratio are important indicators. The eutrophication problems in the Yibin section of Yangtze River, nitrogen is the limiting factor of eutrophication due to the low TN/TP ratio (4.05:1) [10]. While nitrogen should be considered as the limiting factor when TN/TP is less than 10:1. When the discharge of nitrogen was increased and the temperature was in the range of 20.0 to 25.0ºC, the algae proliferation rate is accelerated and river eutrophication became high [10]. For the eutrophication problems in the Liujiang River, TN/TP ratio was higher than 16.0, which indicated that TP was the restrictive factor for eutrophication problems [11]. The fluxes of nutrient elements in different periods, reflecting the accumulation of eutrophication over time, can illustrate the level of eutrophication in the whole river basins [12, 13]. The fluxes of nutrient elements can reveal the transportation processes in the river basin and its geochemical cycling processes. Powers et al compared the phosphorus fluxes of the Yangtze River, the Thames River, and the Maumee River, indicating that phosphorus was accumulated long after inputs and might continue to release by balance calculation of input and output flux over the past 30-70 years [14]. Also, the relationship between the concentration or fluxes of nutrient elements and other environmental indexes, e.g. river runoff flows, total suspended substance, can illustrate the fate of eutrophication [15, 16]. In the statistical analysis of the fluxes, the product of average period-concentration and average period-flow was the common method, which emphasizes the role of total runoff during the period, suitable for situations where non-point sources dominated. Yang et al. estimated TN and TP fluxes in the Yangtze River using the product of average period-concentration and average period-flow, showing that the period-averaging method was the selected optimal estimates for dissolved fluxes, better than other methods by 0.09-49.75% [17].

Eutrophication of river basins is a complex and multi-dimensional process, which means that there is no single variable index that can reflect the state of eutrophication [18]. For the study of eutrophication in large-scale overall river basins, it needs not only a large number of monitoring indicators but also the spatial analysis of river eutrophication levels. The geographic information system (GIS) provides an important tool for the comprehensive analysis of river basins' eutrophication. The GIS can synthesize the eutrophication presented by various parameters and form a thematic map that can illustrate the spatial distribution of river basins' eutrophication status. Ahmed et al investigated the spatial distribution of the eutrophication status of Manzara lake via the inverse distance weighted (IDW) interpolation method to describe the environmental status of the lake [19]. The application of regression in GIS can be used to assess the sensitivity of small rivers to eutrophication [20]. In addition, the integration of the GIS and remote sensing can be used to visualize the nutrient elements pollution monitoring system to achieve dynamic measurements of nutrient elements pollution indicators [21]. Therefore, the spatial analysis method within a large-scale river basin will provide a powerful assistant for river basins' eutrophication studies to solve spatially complex and tempora differences.

Eutrophication is also a serious problem in the Pearl River basin [22-24]. Wei et al. investigated the Guangzhou Section of the Pearl River estuary and found that in February, May, August, and October from 2005 to 2007, the concentrations of dissolved inorganic nitrogen and phosphate were 93.2 to 530.4 $\mu mol \cdot L^{-1}$ and 0.62 to 3.16 $\mu mol \cdot L^{-1}$, respectively, with high TN/TP ratio (57 to 667) [23]. Eutrophication is more serious in the Pearl River estuary, belonging to a medium pollution level [25]. Additionally, the nutritional status quality index in Shenzhen Bay of Pearl River estuary was highest as 22 and 23 in the dry period and flood period [26]. However, the eutrophication problem of each section cannot represent the overall eutrophication level of the Pearl River Basin. As eutrophication elements, nitrogen, and phosphorus, in rivers will also change through sedimentation and retention [27], chemical transformation [28], biological transformation [29], etc., there is no correlation or regularity between nitrogen and phosphorus in the river basin, which leads to differences in the level of eutrophication in the river basin. Therefore, spatio-temporal analysis of basin-wide needs to be applied to the study of eutrophication in the river basins.

The Pearl River, as the third-largest river in China with an annual runoff of more than 300 billion m^3, has serious eutrophication problems [25, 26]. In this paper, (i) statistical analysis was carried out on the river section data of the Pearl River, (ii) the transmission fluxes of the eutrophication elements of the Pearl River Basin were deduced based on the period-averaging method, and (iii) the spatial distribution analysis was formed based on GIS.

Materials and Methods

Study Area

The Pearl River is the third-largest river in China with an annual runoff of more than 300 billion m^3 [25, 26]. It includes the West River, East River, North River, and various rivers on the Pearl River Delta. The East River and North River flow roughly from northeast to southwest, while the West River flows roughly from west to east. All rivers converge in the Pearl River Delta network river area and are finally injected into the South China Sea respectively. The flood period is from April to September of the current year, and the dry period is from October to March of the following year.

Data Collection

The source of water quality data for 2016 - 2018 in this paper is the automatic water quality monitoring platform of the China General Environmental Monitoring Station (www.cnemc.cn). It includes 92 monitoring sections, of which 34 monitoring sections (S1 to S34) are on the mainstream and tributaries of the East River, West River, and North river (Fig. 1). The data are the monthly average data of monitoring sections. The data was filtered to eliminate the extreme values and then the missing points were completed by using the spatial interpolation method in GIS.

The Flux Calculation

The fluxes of nutrient elements are obtained via product of average period-concentration and average period-flow, showing the period-averaging method [30].

$$W = \int_T F(t)dt = \int_T Q(t)C(t)dt \tag{1}$$

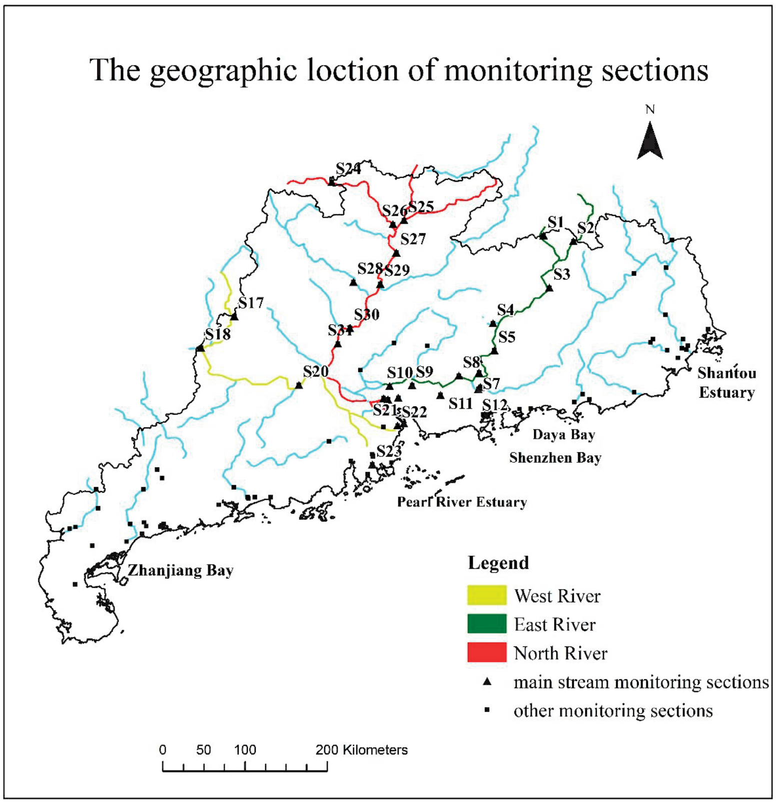


Fig. 1. The geographic location of the water quality monitoring sections in the Pearl River. (Different main streams, West River, East River, North River, presented as yellow, fir green, and red, respectively. S1 - S34 were the water quality monitoring sections in those main streams, presented as "▲". Other monitoring sections were presented as "■").

Table 1. Statistics of TN concentration at the monitoring section of the Pearl River in flood period and dry period of 2016-2018.

Year	Mean Concentration			Range	Quality Standard and Limit of Surface Water Environment					
	Annual	Flood period	Dry period		Case I	Case II	Case III	Case IV	Case V	Poor-quality water
2016	2.56	2.50	2.69	0.10 ~ 22.41	0.74%	4.51%	11.94%	12.55%	19.50%	50.76%
2017	2.93	2.82	3.05	0.13 ~ 35.50	0.39%	4.09%	10.51%	10.96%	21.98%	52.07%
2018	2.86	2.62	3.10	0.02 ~ 41.00	0.52%	1.91%	7.65%	15.99%	23.54%	50.39%

Table 2. Statistics of TP concentration at the monitoring section of the Pearl River in flood period and dry period of 2016-2018.

Year	Mean Concentration			Range	Quality Standard and Limit of Surface Water Environment					
	Annual	Flood period	Dry period		Case I	Case II	Case III	Case IV	Case V	Poor-quality water
2016	0.15	0.15	0.15	0.01 ~ 2.34	6.41%	54.33%	24.08%	7.02%	2.48%	5.68%
2017	0.16	0.15	0.17	0.00 ~ 3.72	6.87%	55.48%	22.88%	4.93%	2.41%	7.70%
2018	0.16	0.15	0.17	0.01 ~ 3.54	7.13%	50.78%	27.91%	5.22%	2.70%	6.26%

$$W = K \frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \overline{Q_r} \quad (2)$$

where W is the flux of nutrient element in the Pearl River; $Q(t)$ is the function of period, and $C(t)$ is the function of the period; Qi is the instantaneous runoff flux; Ci is the instantaneous concentration of the nutrient element; K is adjustable constant; $\bar{Q}\, i$ is the month-average runoff flux.

Spatial Interpolation

Spatial interpolation is a method to calculate unknown spatial data from these discrete spatial data. It is based on the basic assumption of the First Law of Geography [31]. When the mathematical expectation of observation Zi is an unknown constant, the expression for solving the weight coefficient of the Kringing method is as follow:

$$\begin{cases} \sum_{i=1}^{n} \lambda_i Cov(x_i, x_j) - \mu = Cov(x_0, x_i) \\ \sum_{i=0}^{n} \lambda_i = 1 \end{cases} \quad (3)$$

where λi is the weight of each observation; $Cov(xi, xj)$ is the covariance of observation of two points; μ is the Lagrange multiplier, and the covariance $Cov(xi, yi)$ can be expressed by the variogram $\gamma(xi, yi)$. The variance function at this point under the second-order stationary assumption is:

$$\gamma(x_i, y_j) = \frac{1}{2} E[Z(x_i) - Z(x_j)]^2 \quad (4)$$

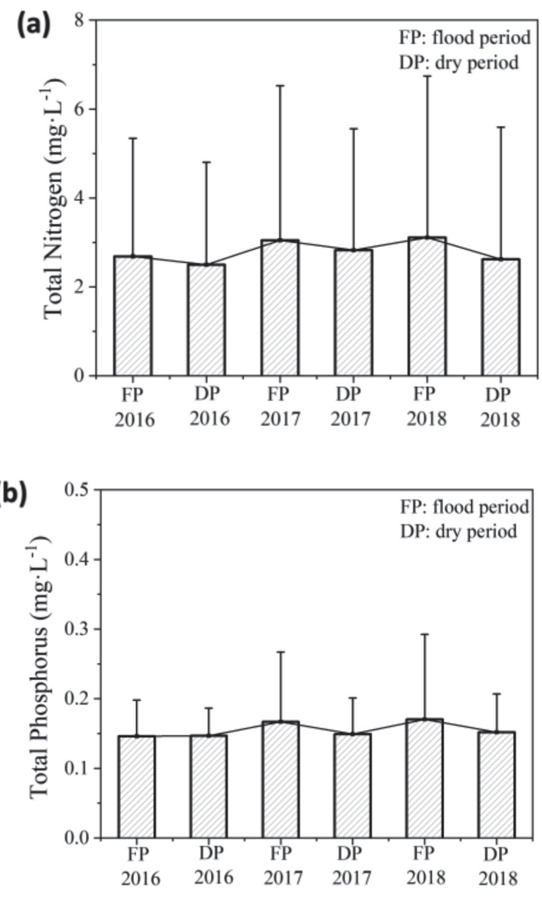


Fig. 2. The average concentration at the monitoring section of the Pearl River in flood period and dry period of 2016-2018. a) TN; b) TP.

The above spatial-temporal analysis methods are implemented by using ArcGIS 10.5.

Results and Discussion

The Characteristic of Eutrophic Elements in Pearl River

The statistical results of nutrient elements in the Pearl River Basin are shown in Tables 1 and 2. The annual mean concentrations of eutrophic elements (TN and TP) in the Pearl River Basin were relatively stable, and both the TN and TP in the dry period were slightly lower than in the flood period, but not significant (Fig. 2). The annual concentration of TN was ranged from 2.56 to 2.93 $mg\cdot L^{-1}$, and that of TP was ranged from 0.15 to 0.16 $mg\cdot L^{-1}$. Obviously, according to the national surface water standards, nitrogen was the eutrophication element exceeding the standard more seriously. Poor-quality water sections for TN were 50.76%, 52.07%, 50.39% from 2016 to 2018, respectively, based on Quality Standard and Limit of Surface Water Environment of China (GB3838-2002). The quality water sections of Case I and Case II were ranged from 0.52% to 0.74% and from 1.92% to 4.51%, respectively. It is demonstrated that more than 80% of sections in the Pearl River Basin were polluted by nitrogen. As to phosphorus, the quality water sections of Case II and Case III were 78.41%, 78.36%, and 78.69% from 2016 to 2018, respectively, which indicated that the water quality of the Pearl River was fine for phosphorus. As to the whole basin, the TN/TP ratio of Pearl River was 24.7, exceeding the most suitable molar ratio for plankton growth with an average of 16, which was an over-enrichment of nitrogen relative to phosphorus [10, 32, 33]. The limitation of low phosphorus would result in excess N being left in the river basin, because of potential limitation both phytoplankton biomass and N utilization [34]. In addition, the range of the concentration of TN and TP varied greatly (Tables 1-2), showing not-normality, and poor-quality water sections had a trend of increasing, which indicated that eutrophic elements pollution sources occurred at some point in the Pearl River basin. The results show that the nitrogen pollution in the Pearl River Basin is very serious, and it is limited by low phosphorus, which poses a threat to the water quality and allocation safety of the Pearl River. There was a certain deterioration trend from 2016 to 2018, so effective measures need to be put forward to control.

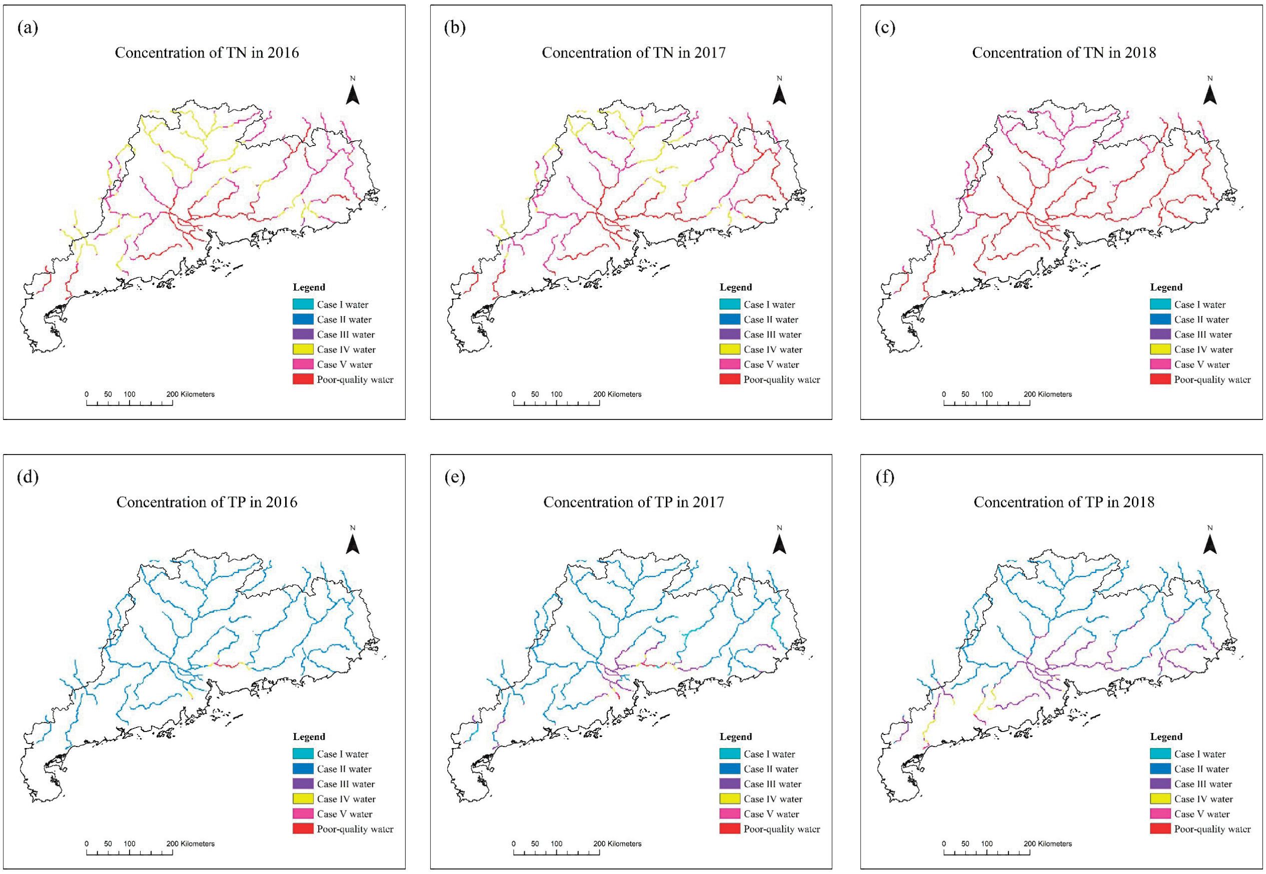


Fig. 3. Spatial distribution of TN and TP in the Pearl River Basin from 2016 to 2018.
The concentration of TN in a) 2016; b) 2017; c) 2018. The concentration of TP in a) 2016; b) 2017; c) 2018.

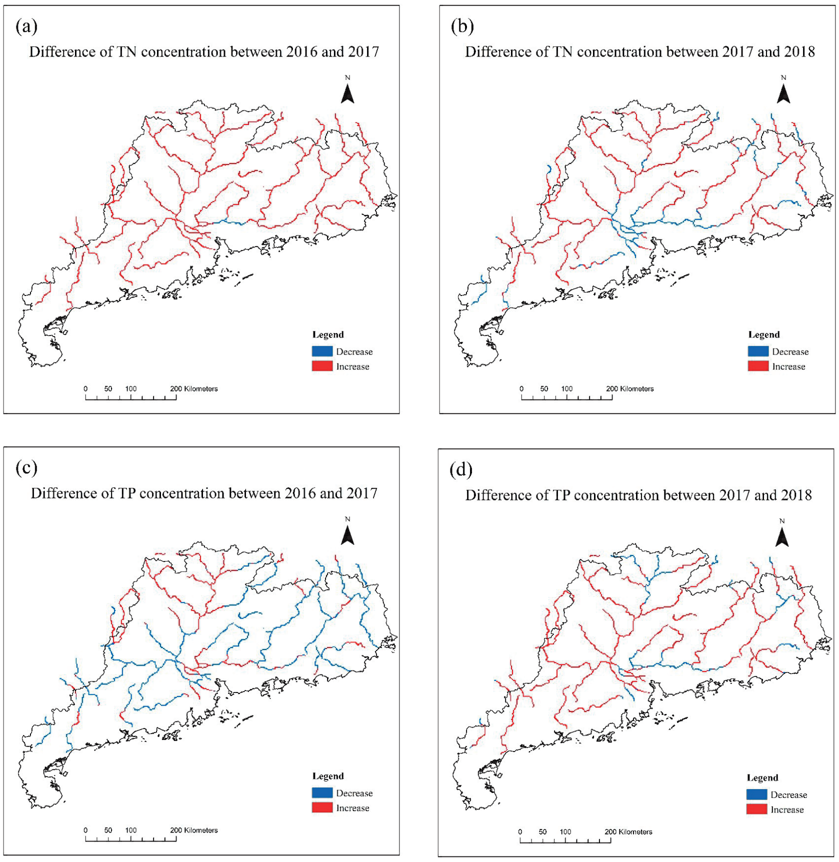
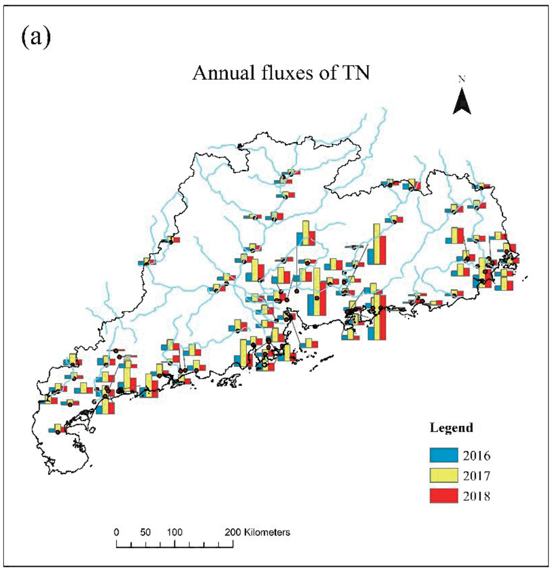


Fig. 4. Annual trends of nutrient concentrations in Pearl River Basin. a) The change in TN concentration between 2016 and 2017. b) The change in TN concentration between 2017 and 2018. c) The change in TP concentration between 2016 and 2017. d) The change in TP concentration between 2017 and 2018.

To explore the spatial-temporal of nutrient elements in Pearl River, ArcGIS was employed to plot the thematic map of the concentrations of nutrient elements. As shown in Figs 3a) and 3c), it exhibits a wide distribution of high concentration, and Case IV or worse water quality accounted for the majority of the Pearl River basin. The most polluted TN in Pearl River Estuary exhibited annual fluctuations, showing an increasing trend from 2016 to 2017 and a slightly decreasing from 2017 to 2018 (seen in Figs 4(a-b)), remaining with poor-quality water. The pollution of TN in the East River was more serious than in the West River and North Rivier, with an average concentration of 2.11±3.61 mg·L^{-1}, respectively. Meanwhile, all of East River, West River, and North River are increasing from 2016 to 2018 (seen in Figs 4(a-b)). It indicated that the nitrogen exceedances of the Pearl River were not caused by any point sources, but the excess input of TN through the Pearl River basin. As to phosphorus, shown in Fig. 3(d-f), Case I and Case II accounts for the majority of the Pearl River basin, with the TP average concentration of 0.12±0.21 mg·L^{-1}. The severely contaminated sections occurred mainly in the Pearl River estuary, and the concentration of TP increased from 2016 to 2018 (seen in Figs 4(c, d). The areas of TP contamination were expanded from 2016 to 2018, including Shantou Estuary, Daya Bay, and Zhanjiang Bay. It was suggested that the point sources of TP were dominant in the estuary, leading to the phosphorous contamination risk. These point sources of pollution were related to the dense urban agglomeration downstream of the Pearl River. In the Pearl River Delta region, the total amount of sewage ranged from 12,000 to 18,000 t/a in 2008-2017 [35], and the sewage discharge was the first contributor to TP in the Pearl River [36].

The Annual Fluxes of Eutrophic Elements

To explore the transportation of the nutrient elements, the fluxes of TN and TP were plotted thematic map via ArcGIS. As shown in Fig. 5, both the fluxes of TN and TP in the Pearl River estuary were significantly higher than those at the upstream monitoring sections, and obviously, the fluxes of TN and TP had increasing trends from upstream to downstream of the Pearl River basin. It indicated that the fluxes of nutrient elements in the Pearl River basin were accumulating throughout the basin. TN transferred from the Pearl River basin to the ocean reached 3.26×10^5, 6.86×10^5, and 4.24×10^5 t from 2016 to 2018, respectively. As to TP, the transportation fluxes were 1.59×10^4, 2.84×10^4, and 1.99×10^4 t,



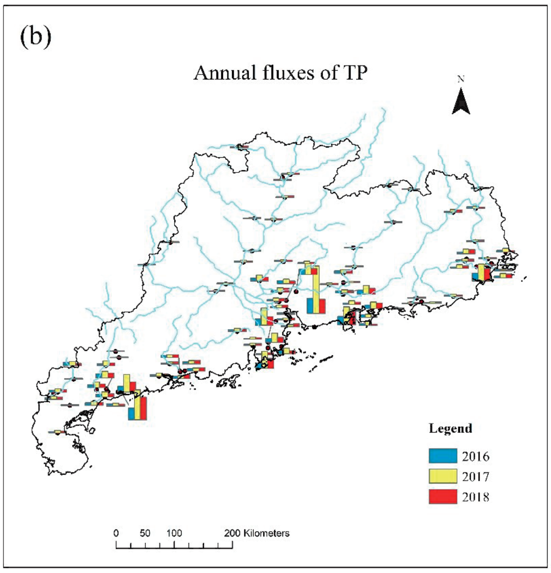


Fig. 5. Spatial distribution of annual cumulative TN and TP in the Pearl River Basin from 2016 to 2018. a) TN; b) TP.

respectively. The fluxes of TN and TP were the highest in 2017, while the annual change was not significant. The fluxes of TN and TP were closed to other literature. According to the study of Wang et al, the average fluxes of TN and TP transferred from the Pearl River basin to the ocean were 7.47×10^5 and 1.48×10^4 t from 1997 to 2017, respectively [37]. And in 2005-2006, it was estimated by the study of Lu et al., TN and TP transfer from the Pearl River basin to the ocean were 6.97×10^5 and 2.39×10^4 t, respectively [38]. In addition, according to the Bulletin of Guangdong Marine Environmental Status (http://gdee.gd.gov.cn), 530,300 t dissolved inorganic nitrogen and 43,500 t TP were estimated to discharge in the Pearl River [39]. Therefore, the fluxes of TN and TP transferred from the Pearl River basin to the ocean exceed 10^5 and 10^4 t/a in recently 2 decades, which imposed a huge impact of eutrophication on the ocean.

Due to the strong interference of human activities and the strong coupling between land and sea, the input and output of estuarine material resources have changed greatly, resulting in the fragility and sensitivity of the estuarine ecosystem, therefore, the estuarine flux should be paid more attention [40, 41]. From the flux thematic map (Fig. 5), Pearl River Estuary was the most transportation of TN and TP among these estuaries. TN transferred from the Pearl River Estuary to the ocean were 1.29×10^5, 2.71×10^5, and 1.93×10^5 t, which occupied 39.4%, 39.5%, and 45.4% of the fluxes of the Pearl River basin from 2016 to 2018, respectively. It indicated that the Pearl River Estuary was the dominant regional transportation of nutrient elements source of the Pearl River basin, which need to control the discharge of TN and TP. The phosphorus in the estuary is different from that in the basin, where the phosphorus will be deposited in the estuary and become a "phosphorus source", posing a threat to the estuary and the ocean [42]. The phosphorus in the estuary may be released into the water body with the transformation of sediments, such as Fe^{2+}/Fe^{3+} [43]. As a phosphorus limited basin, the Pearl River needs to be vigilant about the deposition and release mechanism of phosphorus in the estuary.

Further from the fluxes of different mainstream, East River, West River, and North River had different characteristics of the transportation of TN and TP. As shown in Fig. 6a), the flux of TN in the East River upstream was relatively maintained stable, and only increased slightly in monitoring section S9 due to the confluence of tributaries. Due to water self-purification, such as denitrification and nitrification, it may cause a decrease of the fluxes of TN in monitoring section S10 [44]. But after monitoring section S13, the flux of TN showed a rapid increase. The monitoring sections S13 to S16 are near the Pearl River estuary, which was the most seriously polluted area and also was the confluence of North River and East River. The TN fluxes of this confluence were 2.87×10^4, 6.07×10^4, and 4.44×10^4 t transferred to the Pearl River estuary from 2016 to 2018, respectively. However, the flux of TN in the North River upstream was relatively high. As shown in Fig. 6c), unlike the fluxes of TN of East River and North River, the TN flux of West River did not change rapidly. The TN flux of West River upstream presented a higher trend and was maintained stably, without decreasing or increasing due to water self-purification or pollution increased. The TN fluxes of West River were 1.57×10^4, 3.38×10^4, and 2.68×10^4 t transferred to the Pearl River estuary from 2016 to 2018, respectively (Figs 6(a, c, e)). Therefore, the discharge of nitrogen needs to be controlled in the West River and North River. As to the fluxes of TP, it was at the low level of transportation in the West River and North River, while different in the East River (seen in Figs 6(b, d, f)). The fluxes of TP trends

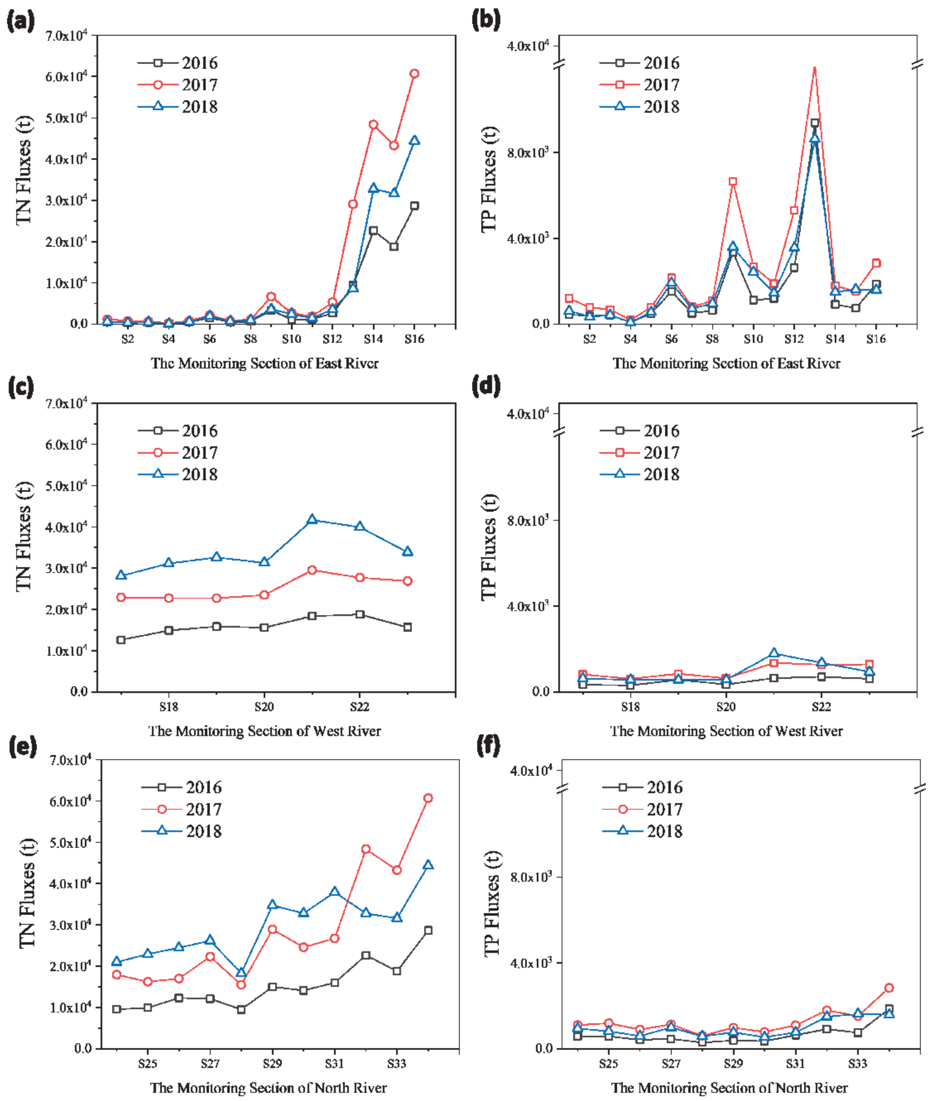


Fig. 6. The trends of nutrient fluxes in the mainstream of the Pearl River along the stream monitoring sections. a) The TN fluxes of East River; b) The TP fluxes of East River; c) The TN fluxes of West River; d) The TP fluxes of West River; e) The TN fluxes of North River; f) The TP fluxes of North River.

in East River were obvious fluctuations. Before the monitoring sections of S6, S9, and S13 may exist severe point source pollution of phosphorus, leading to a rapid increase of TP flux. While, possibly due to the water self-purification or deposition, the TP fluxes of the following monitoring sections were decreased rapidly. In some confluence of rivers, the deposition of phosphorus can occur, leading to a rapid decrease in the flux of TP [42]. However, the East River was still the mainstream of the Pearl River that discharge the most phosphorus, and there is also a risk of long-term release of deposited phosphorus. Therefore, the discharge of phosphorus needs to be controlled in the East River.

Correlation between Eutrophic Elements and Water Quality

It was illustrated that the eutrophication in the Pearl River basin was mainly dominated by TN, while TP was only slightly polluted, from both the thematic maps of concentrations and fluxes. The relationship of TN and TP in Pearl River was significant (non-normality, Spearman $p<0.01$), with 0.814 of the correlation coefficient. The ratio of TN/TP was 24.7 (>16.0) (Table 3), which indicated that phosphorous is the restrictive factor of eutrophication of the Pearl River Basin [11]. As to East River, West River, and North River, the relationships of TN and TP were all significant, with 0.830, 0.839, and 0.631 of the correlation coefficient, respectively. And The ratio of TN/TP in East River, West River, and North River were 32.5, 34.7, 28.9, respectively, which also indicated that phosphorous is the restrictive factor of eutrophication (Table 3).

Eutrophication, presented as the algal blooming caused by exceeding nutrient elements, can increase the chemical oxygen demand (COD) and decrease the total dissolved oxygen (DO) in the water [45, 46].

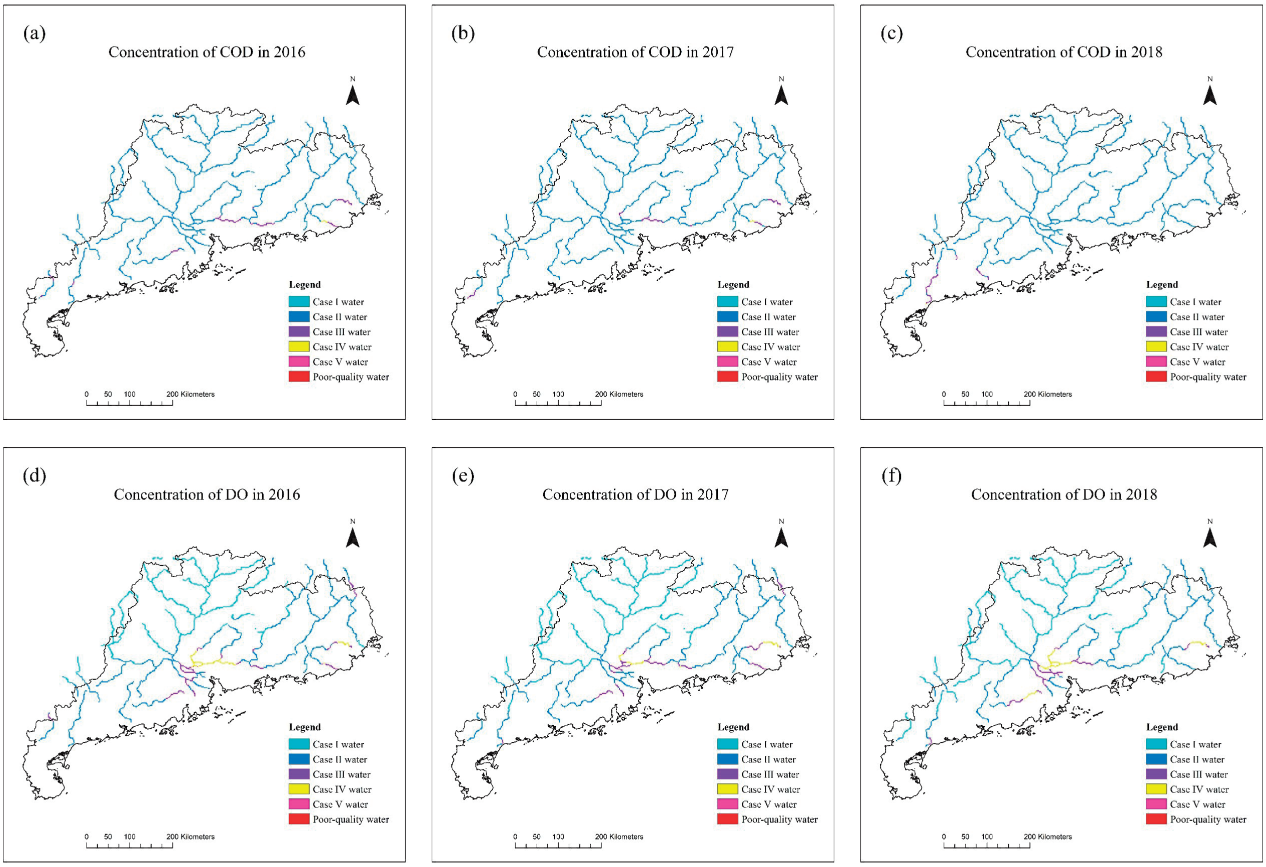


Fig. 7. Spatial distribution of COD and DO in the Pearl River Basin from 2016 to 2018. The concentration of COD in a) 2016; b) 2017; c) 2018. The concentration of DO in a) 2016; b) 2017; c) 2018.

As shown in Figs 7(a-c), the COD of the Pearl River basin remained as Case III or better, with the annual average concentration of 13.24, 12.73, and 12.54 $mg \cdot L^{-1}$, respectively. Also, except Pearl River estuary and upstream of the North River, the concentration of COD was decreased from 2016 to 2018 (seen in Figs 8(a,b)). It indicated that eutrophication did not cause the rapid increase of COD. It may be the high ratio of TN/TP that limited biological activities, resulting in decreasing in COD. While, as shown in Figs 7(d-f), Case III and Case IV account for the downstream of the Pearl River basin based on the concentration of DO, which showed a serious effect of eutrophication, and the concentration of DO decreased significantly from 2016 to 2017 (seen in Figs 8(c,d)). It indicated that eutrophication caused a rapid decrease in DO.

In addition, the relationships between COD or DO and nutrient elements are figured out to explore the biochemical behaviors of TN and TP in Pearl Rivers Basin. As to the whole Pearl River basin, TN and TP are positively correlated with COD, with a correlation coefficient of 0.597, 0.685 (non-normality, Spearman $p<0.01$), and negatively correlated with DO, with a correlation coefficient of –0.731, –0.769 (non-normality, Spearman $p<0.01$). It demonstrated that eutrophication pollution was affected by nitrogen and phosphorus in the Pearl River basin, though the concentration of COD was not high. As for the three main streams of the Pearl River Basin, the correlations of East River with COD and DO were the same as the Pearl River basin. TN and TP are positively correlated with COD, with a correlation coefficient of 0.796, 0.903 (non-normality, Spearman $p<0.01$), and negatively correlated with DO, with a correlation coefficient of –0.859, –0.860 (non-normality, Spearman $p<0.01$) (Table 3). While TN and TP showed no significant correlation between COD in the West River but exhibited a significant negative correlation for DO, with a correlation coefficient of –0.670, –0.820 (non-normality, Spearman $p<0.01$). It speculated that the West River was not dominated by eutrophication pollution due to water self-purification. As to the North River, the correlation coefficient between TN and COD was 0.46 (non-normality, Spearman $p<0.01$), and no significant correlation between TP and COD, which was lower than the Pearl River basin. TN and TP are negatively correlated with DO, with a correlation coefficient of –0.894, –0.718 (non-normality, Spearman $p<0.01$). It indicated that the eutrophication of the North River was dominated by nitrogen, while the total phosphorus showed a weak impact on eutrophication.

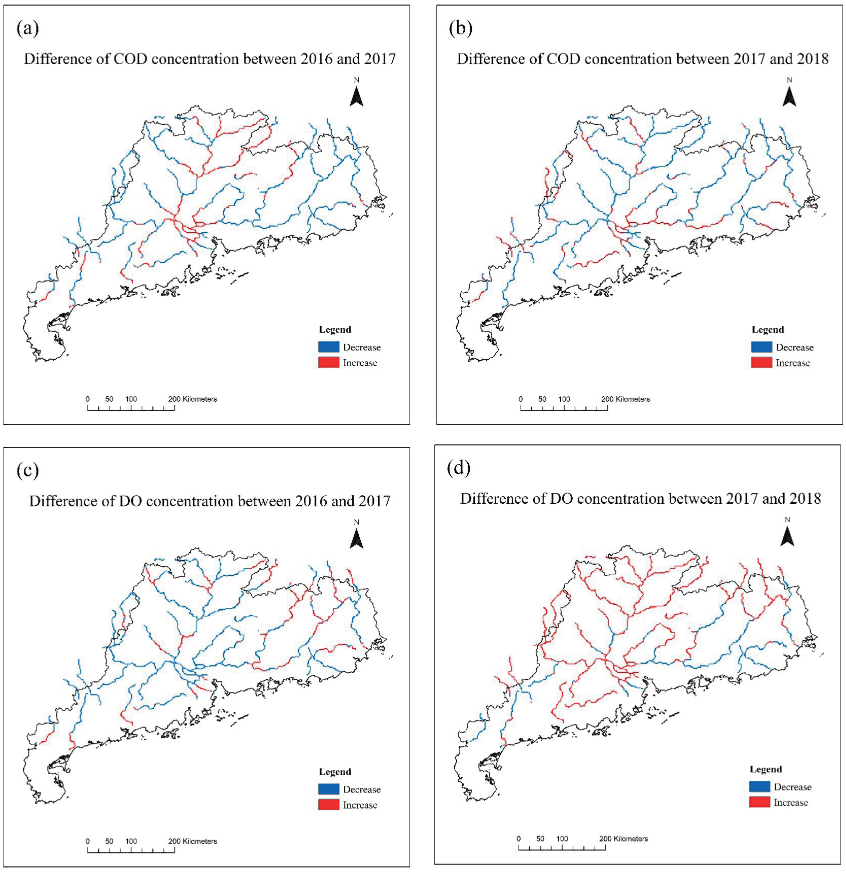


Fig.8. Annual trends of COD and DO in Pearl River Basin. a) The change in COD concentration between 2016 and 2017. b) The change in COD concentration between 2017 and 2018. c) The change in DO concentration between 2016 and 2017. d) The change in DO concentration between 2017 and 2018.

Table 3. The Spearman correlation between TN, TP, COD, and DO.

Rivers	Ratio of N/P	Correlation coefficient			
		TN and COD	TP and COD	TN and DO	TP and DO
East River	32.5	0.796**	0.903**	-0.859**	-0.860**
West River	34.7	-0.269	-0.049	-0.670**	-0.820**
North River	28.9	0.465**	0.319	-0.894**	-0.718**
Pearl River	24.7	0.597**	0.685**	-0.731**	-0.769**

Note: ** indicates the 0.01 significance test and * indicates the 0.05 significance test.

Conclusion

This study summarized and analyzed the temporal and spatial distribution characteristics of nutrient elements concentrations in the Pearl River basin. Nitrogen showed a dominating position while phosphorus pollution was relatively light on the eutrophication in the Pearl River basin. In 2016-2018, the concentration of TN and TP changed steadily, and the dry period are slightly lower than in the flood period. The Pearl River estuary was the most polluted area of nutrient element concentration and an increasing trend was exhibited. This study also calculated and analyzed the fluxes of TN and TP in the Pearl River basin and the mainstreams. It indicated that the Pearl River estuary was the major channel for the transportation of nutrients in the Pearl River basin. The study of pollutant fluxes and distributions in the Pearl River basin were essential for clarifying the causes of eutrophication and also providing data and theoretical support for further water pollution control.

In addition, there is a significant correlation between TN and TP in the Pearl River basin. The annual average TN/TP ratio is 24.7, which indicated that the main limiting factor for eutrophication pollution in the Pearl River basin was phosphorus. The control of algae blooming in the Pearl River basin should be combined with restrictive factors. Due to the relationship between COD or DO and nutrient elements, as to the mainstream of the Pearl River basin, the North River was dominated by nitrogen while the pollution in the West River was not mainly eutrophication.

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Conflict of Interest

The authors declare no conflict of interest.

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