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Assessment of Water Quality Evolution in the Pearl River Estuary (South Guangzhou) from 2008 to 2017

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Abstract: To control the water pollution in the Pearl River Estuary (PRE), a series of measures have been enacted in recent years. The efficacy of these measures on water quality improvement is, however, currently unknown. To evaluate the variation of water quality in response to the pollution control measures in the PRE during the last decade (2008–2017), our study conducted a long-term monitoring program of estuarine water in the representative city Guangzhou that targeted fecal coliform (F. Coli), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD_{Cr}), potassium permanganate index (COD_{Mn}), petroleum, total nitrogen (TN), ammonia nitrogen (NH_3–N) and total phosphorus (TP). In the last decade, F. Coli, BOD_5, COD_{Cr} and COD_{Mn}, petroleum and NH_3–N have shown a significant reduction by 78.8%, 50.9%, 37.5%, 18.9%, 75.0% and 25.0%, respectively. In contrast, TN and TP remained stable. Water quality index calculations indicated that the water quality was elevated from the marginal–fair level to the good level, particularly after 2012. The biochemical pollutants and nutrients in the estuarine water most likely originated from the upper river due to the wastewater discharge, fecal pollution and agricultural input. The success of pollutant reduction could thus be attributed to industrial upgrading and relocation, as well as the improvement of the sewage treatment system in Guangzhou. However, efficient approaches to reduce TN pollution should be implemented in the future.

Keywords: temporal variation; biochemical pollutant; nutrients; water quality index; pollution control; Pearl River Estuary

1. Introduction

Estuaries often suffer from the serious problem of water pollution due to growing populations, urbanization, and industrialization [1,2]. Pollutant transport through estuaries to oceans plays an important role in the global geochemical cycling of pollutants and often poses a great risk to the ecosystem in coastal and oceanic zones [3,4]. For instance, the large quantity of organic pollutants discharged into estuarine water threatens aquatic life because of the depletion of dissolved oxygen in water by aerobic decomposition [5]. Pathogenic bacteria derived from domestic and livestock wastewater lead to public health problems in densely populated coastal cities [6]. In addition, the high concentration of nutrients in coastal and seawater results in eutrophication and the proliferation of harmful algae [7,8]. Therefore, it is necessary to monitor the biochemical pollutants and nutrients in estuarine water in order to take abatement actions to prevent the deterioration of water quality and assess the efficacy of pollution control measures.

The Pearl River Estuary (PRE) is situated in the subtropical region of Guangdong in South China that opens to the Ling Ding Bay and the northern part of the South China Sea [9]. The Pearl River Delta (PRD) is one of the most developed areas in China, and many large cities (e.g., Guangzhou, Shenzhen, Hong Kong, and Macao) are clustered there. The PRD has been undergoing rapid urban expansion and economic development since the implementation of reform and the opening-up policy of China in 1978 [1]. As a result, the PRE has become quickly polluted due to its dense population and industrial development [10–12]. Numerous wastewaters have been directly discharged from the urban area to the Pearl River with insufficient treatment [13]. In sewage outlets into the sea, the water parameters often exceed regulated limits, including chemical oxygen demand (COD_{Cr}), biochemical oxygen demand (BOD_5), ammonia nitrogen (NH_3–N) and total phosphorus (TP) [14]. The sewage flow through the inner shore rivers has resulted in the deterioration of water quality in nearshore and offshore seawaters [15]. Eutrophication is one of the most serious environmental problems in the PRE due to the accelerated inputs of anthropogenic nutrients [16–18].

The public and the government first started to be concerned about the pollution problem in the PRD in the 1980s [19]. In particular, a series of pollution abatement measures to control water pollution have been implemented in Guangzhou (the capital city of Guangdong Province). In 1989, the first wastewater treatment plant (WWTP) in the PRE was built in Guangzhou. Since the 2000s, water pollution control became one of the most important issues in the public eye and has become a priority of government work in Guangzhou. From 2008 to 2017, efforts have been made in the improvement of wastewater collection networks and the construction and upgrading of WWTPs. Heavily polluted factories have been forced to move out of Guangzhou [20]. The pollution from livestock and poultry breeding industries has also become more heavily regulated and inspected [21]. Remediation strategies, such as river dredging and sewage interception, have been taken to restore polluted rivers. However, the efficacy of these pollution control measures is still of great concern by the public. For example, several cleaned black-odor rivers have been found to easily revert to their polluted state very soon after cleaning [22].

Previous studies have mainly focused on the impact of urbanization and industrialization on the deterioration of water quality in the PRD at a large scale [10,11,13,23]. However, little attention has been paid to the recovery of the estuarine system in response to ongoing pollution control measures in recent years. Though historical data on water quality variation in the PRE could be obtained from the literature, it is difficult to reach a solid conclusion through a comparison of water quality parameters from different past studies due to the inconsistency in sampling sites, sampling seasons, monitoring parameters, and analysis methods. Therefore, it is necessary to conduct a long-term monitoring program on parameters that indicate water quality variation in the PRE.

The main objectives of our study were as follows: (1) To track the long-term (2008–2017) temporal trends in different water pollution parameters from south Guangzhou based on a monthly monitoring program and (2) to assess the water quality variation in south Guangzhou over the last decade with an eligible water quality index. This work is expected to provide new insights into the evolution of water quality and the influence of water control measures in the PRE region in the last decade.

2. Materials and Methods

2.1. Study Area

The Pearl River is the second largest river in China, and it receives water from the East River, the West River and the North River, finally flowing into the South China Sea. Guangzhou is the provincial capital city with the longest development history in Guangdong, which is in the center of the PRE near the entrance of the Ling Ding Bay. The urbanization rate of Guangzhou is high (86.14%), and the population density is about 1950 persons per km^2. The area has a subtropical monsoon climate, and the temperature ranges from 9 to 29 °C annually [9]. The rainy season spans from April to September, and the dry season lasts from October to March, with an annual average precipitation of about 1720 mm [10].

To investigate the influence of the pollution control measures employed by the Guangzhou government on the water quality in the estuarine zone, Nansha, the southeast district of Guangzhou, was selected as the target area (~400 km^2). The topography of Nansha has been strongly modified over the last century by the land reclamation of tidal wetlands. The newly reclaimed area has been used for agriculture, industry and port transportation, resulting in an increasing number of residents and increasing discharge of industrial and domestic wastewater [24]. The local hydraulics are primarily affected by Pearl River runoff and South China Sea tides. The sea tides reciprocating north and south in the study area are weak, with an average tide difference of 1.2–1.6 m [25]. Two outlets of the Pearl River, Jiao Men and Hong Qili, were part of this study area and account for 23.7% of the total runoff into the South China Sea.

2.2. Sampling Methods

A total of six sites (Xiaohu (XH), Tingjiaodaqiao (TJDQ), Nanheng (NH), Lixinsha (LXS), Hongqili (HQL) and Jiaomen (JM)) comprised our monitoring networks in channels or outlets of the Pearl River in Nansha, south Guangzhou (Figure 1). From 2008 to 2017, water samples were collected monthly from the monitoring sites following the "Technical Specifications Requirements for Monitoring of Surface Water and Waste Water (HJ/T 91-2002)." During the monthly sampling event at each monitoring site, surface water (0.5 m from the river surface) and bottom water (0.5 m from the river sediment) samples were collected during the flood tide and ebb tide within one day. For petroleum analysis, surface water was individually collected 0–0.3 m under the surface. The preservatives, storage time, storage conditions and sampling containers used for water samples are provided in the Supplementary Materials (Table S1).

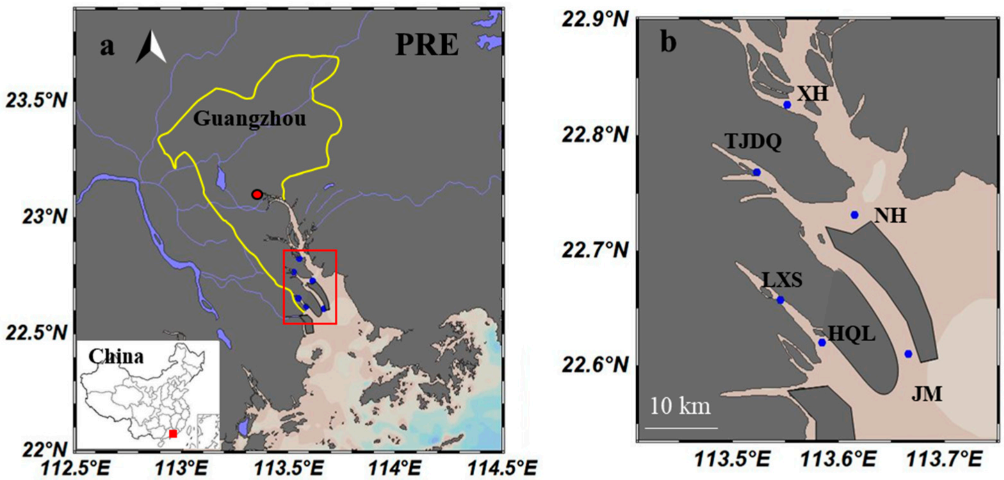

Figure 1. Locations of sampling sites (blue points) on the Pearl River Estuary (**a**) and Nansha, South Guangzhou (**b**) maps (created by Ocean data view).

2.3. Water Quality Parameter Analysis

A total of 11 water quality parameters were selected for analysis, including a microbiological parameter: fecal coliform (F. Coli); physiochemical parameters: T, pH, dissolved oxygen (DO), potassium permanganate index (BOD_5), COD_{Cr}, potassium permanganate index (COD_{Mn}), and petroleum; and nutrients: total nitrogen (TN), NH_3–N, and TP. The physicochemical parameters, DO, BOD_5, COD_{Cr} and COD_{Mn}, are common indicators of organic pollution in water [26,27]. Petroleum was selected as a representative local organic pollutant because the petrochemical industry is a pillar industry of Guangzhou [28]. The full name, units, and analytical methods for these water quality parameters are summarized in Table 1. T, pH and DO were measured on site, and the other parameters were measured in our laboratory.

Table 1. Summary of the units, analytical methods and detection limits of different parameters in water.

Parameters	Full Name	Units	Analytical Methods	Standards	Detection Limits
F. Coli	Fecal coliform	CFU L^{-1}	Multi-tube zymolytic method/membrane filter method	[a]	-
T	Temperature		Thermometer method	GB13195-91 [b]	-
pH			Glass electrode	GB6920-86 [b]	-
DO	Dissolved oxygen	mg L^{-1}	Iodimetry	GB11913-89 [b]	0.2
BOD_5	Five-day biochemical oxygen demand	mg L^{-1}	Dilution and inoculation test	GB7488-87 [b]	2
COD_{Cr}	Chemical oxygen demand	mg L^{-1}	Dichromate method	GB11914-89 [b]	10
COD_{Mn}	Chemical oxygen demand	mg L^{-1}	Permanganate method	GB11892-89 [b]	0.5
Petroleum	Petroleum	mg L^{-1}	Infrared spectrophotometry	GB/T 16488-1996 [b]	0.01
TN	Total nitrogen	mg L^{-1}	Alkaline potassium persulfate digestion-UV spectrophotometry	GB11894-89 [b]	0.05
NH_3–N	Ammonia nitrogen		Salicylic acid spectrophotometry	GB7481-87 [b]	0.01
TP	Total phosphorus	mg L^{-1}	Ammonium molybdate spectrophotometry	GB11893-89 [b]	0.01

[a] Water and wastewater monitoring and analysis method (third edition), China Environmental Sciences press, 1989.
[b] The State Environmental Protection Administration of China, the China National Environmental Monitoring Center.

2.4. Water Quality Assessment

The water quality index is an effective tool for assessing water quality and has been widely used in water management. The Canadian Council of Ministers of the Environment water quality index (CCME-WQI) is one of the most popular indices used in different countries [29]. The CCME-WQI comprises three factors (F_1, F_2 and F_3), reflecting the extent of water quality guideline noncompliance, the frequency of deviation, and the amplitude of deviation, respectively. The mathematical formulation of the CCME-WQI is shown in Equation (1) [30]:

$$\text{CCME-WQI} = 100 - \frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \quad (1)$$

where F_1 represents the percentage of parameters whose guidelines are not met at least once, relative to the total number of parameters measured; F_2 represents the percentage of individual tests that do not meet their respective guideline ("failed tests"); and F_3 is the amount by which the failed test values do not meet their respective guideline. A scaling factor of 1.732 is introduced to scale the index from 0 to 100. The detailed calculation process for F_1, F_2 and F_3 has been clearly described in a previous study [30].

In this study, we used the CCME-WQI to evaluate the water quality from six sites from 2008 to 2017. The target for each parameter was set as follows: F. Coli was 10,000 CFU L^{-1}, pH was 6–9, DO was 5 mg L^{-1}, BOD_5 was 5 mg L^{-1}, COD_{Cr} was 20 mg L^{-1}, COD_{Mn} was 6 mg L^{-1}, petroleum was 0.05 mg L^{-1}, TN was 1 mg L^{-1}, and TP was 0.2 mg L^{-1}, according to the Chinese Environmental Quality Standard for Surface Water Class III (GB3838-2002). The Class III standard from this is designed for centralized drinking water sources, fisheries and swimming, which was suitable for assessing the water quality in the study area. The obtained CCME-WQI ranged from 0 to 100 and was classified into five categories including excellent (95–100), good (80–94), fair (60–79), marginal (45–59) and poor (0–44) [29,30].

2.5. Statistical Analysis

The temporal trends of water quality parameters were analyzed with a simple regression model at the scale of the whole study area. This was achieved by averaging the water quality parameters obtained from the six sampling sites. The minimum, maximum and mean values for each water quality parameter in each year at the scale of the whole study area were summarized by analyzing all of the data collected from the six sampling sites in one year. This analysis was carried out by using Microsoft Excel 2016. The correlation analysis for different parameters was conducted with the SPSS 18.0 statistical package (SPSS Inc., Chicago, IL, USA), and the results are presented in the Supplementary Materials (Table S2).

3. Results

3.1. Distribution of Water Quality Parameters in Different Years

3.1.1. Microbiological and Physiochemical Parameters

During the ten-year study period, the monthly variation in F. Coli and physiochemical parameters in the surface and bottom water in the study area is shown in Figure 2, and a statistical summary of these data is supplemented in Table 2. The Chinese environmental quality standards for surface water are provided in Table 3.

In estuaries, flood and ebb tides normally lead to the mixing of inland riverine water with seawater from the surrounding bay as well as the surface and bottom water [31,32]. In our study, the concentrations of F. Coli and physiochemical parameters in the surface and bottom water were generally consistent during flood and ebb tides (Figure 2), suggesting that the effect of tides on hydrological exchange in the sampling sites was very weak.

For F. Coli, the concentration was initially high in 2008 (annual mean (C_{mean}) = 14,956 CFU L^{-1}, Class IV), then decreased greatly and varied at a low level afterward (C_{mean} = 4294 CFU L^{-1}, Class III). The concentration of DO showed large monthly variation and displayed a slight increasing trend from 2008 to 2017. The level of annual mean DO in the estuarine water belonged to Class II (Table 2).

For BOD_5, the concentration was relatively high from 2008 to 2009 (C_{mean} = 3.01 mg L^{-1}, Class III) and rapidly decreased from mid-2010 on, remaining relatively stable afterwards (C_{mean} = 1.72 mg L^{-1}, Class I). The concentration of COD_{Cr} was high in the years 2010 and 2011 (C_{mean} = 15.7 mg L^{-1}, Class III), and then gradually decreased from 2012 to 2017 (C_{mean} = 7.53 mg L^{-1}, Class I). For COD_{Mn}, the concentration also decreased over the last decade, and the variation was small. The concentration of petroleum maintained at a high level from 2008 to 2012 (C_{mean} = 0.06 mg L^{-1}, Class IV), then rapidly decreased from mid-2012 on, maintaining at a low level from 2013 to 2017 (C_{mean} = 0.02 mg L^{-1}, Class I).

These results showed a clear decreasing trend in organic pollution in our test region and an improvement of water quality in the estuarine water from 2008 to 2017. Specifically, there was a remarkable decrease in the annual mean of F. Coli (by 78.8%), BOD_5 (by 50.9%), COD_{Cr} (by 37.5%), COD_{Mn} (by 18.9%) and petroleum (by 75.0%). No clear seasonal variation pattern of organic pollutants (BOD_5, COD_{Cr}, COD_{Mn} and petroleum) was found in comparison with the monthly rainfall data. This indicated that the anthropogenic activities (e.g., wastewater discharge, agricultural sewage) instead of natural rainfall dominated in the variation of pollutants in the estuarine water from south Guangzhou during the study period.

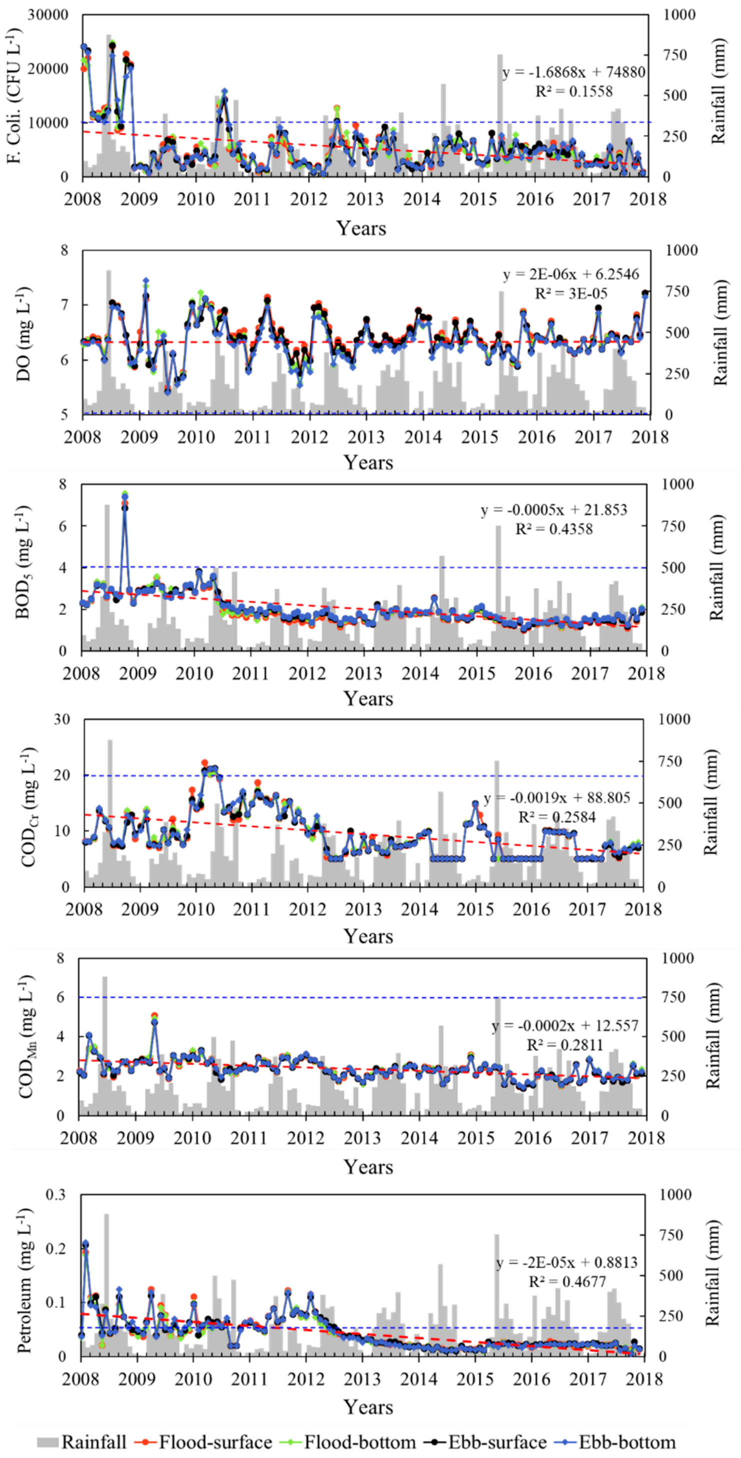

Figure 2. Temporal changes in fecal coliform (F. Coli), dissolved oxygen (DO), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD_{Cr}), potassium permanganate index (COD_{Mn}) and petroleum in the estuarine water measured from six sites (given as mean) in Nansha, Guangzhou, over the ten-year period (2008–2017). Rainfall data are presented as the background information. The red dashed lines refer to the trendlines with equations and R^2 provided. The blue dashed lines refer to the Chinese environmental quality Class III standards for surface water.

Table 2. Summary of statistical analyses for microbiological parameters, physiochemical parameters, and nutrients in water from the Pearl River Estuary (South Guangzhou).

Year		F. Coli CFU L^{-1}	DO mg L^{-1}	BOD_5 mg L^{-1}	COD_{Cr} mg L^{-1}	COD_{Mn} mg L^{-1}	Petroleum mg L^{-1}	TN mg L^{-1}	NH_3–N mg L^{-1}	TP mg L^{-1}
2008	Min	500	4.64	2.00	5.24	1.41	0.00	1.04	0.01	0.01
	Max	35,000	7.42	13.50	34.30	4.96	0.34	4.12	1.36	0.28
	Mean	14,956	6.41	3.06	9.87	2.59	0.08	2.53	0.20	0.09
	SD	9669	0.80	1.54	3.44	0.66	0.06	0.67	0.25	0.03
2009	Min	30	3.10	2.00	5	1.55	0.02	1.30	0.02	0.02
	Max	24,000	7.90	7.10	34.60	6.44	0.19	5.59	1.58	0.25
	Mean	3262	6.22	2.96	9.75	2.83	0.06	2.80	0.25	0.10
	SD	3582	0.73	1.01	4.27	0.92	0.03	0.91	0.21	0.03
2010	Min	50	4.91	1.20	10.00	1.50	0.02	1.83	0.02	0.05
	Max	24,000	7.90	7.00	26.70	4.30	0.29	5.78	1.24	0.26
	Mean	5654	6.60	2.54	16.37	2.55	0.05	3.25	0.32	0.10
	SD	6083	0.53	0.98	5.81	0.54	0.03	0.81	0.24	0.03
2011	Min	20	4.38	0.90	6.11	1.50	0.02	0.97	0.02	0.04
	Max	24,000	7.74	4.50	24.00	4.40	0.13	4.51	1.43	0.52
	Mean	3728	6.31	1.76	15.15	2.65	0.07	2.29	0.30	0.10
	SD	4326	0.60	0.57	7.79	0.51	0.02	0.61	0.24	0.03
2012	Min	20	4.88	0.70	5.00	1.10	0.02	0.97	0.01	0.01
	Max	35,000	7.71	3.90	19.30	4.40	0.17	2.92	1.10	0.29
	Mean	4865	6.33	1.58	9.61	2.31	0.06	1.87	0.27	0.10
	SD	5671	0.47	0.55	5.57	0.59	0.03	0.46	0.22	0.04
2013	Min	10	5.55	0.80	5.00	0.70	0.01	1.34	0.02	0.01
	Max	24,000	7.34	3.70	16.10	3.70	0.06	4.16	0.91	0.19
	Mean	4089	6.40	1.77	7.24	2.23	0.02	2.19	0.19	0.08
	SD	4158	0.32	0.68	3.90	0.53	0.01	0.47	0.16	0.03
2014	Min	130	5.31	1.00	5.00	1.20	0.01	0.13	0.01	0.03
	Max	54,000	7.45	3.80	18.80	4.90	0.03	3.36	0.84	0.20
	Mean	4922	6.43	1.78	7.09	2.27	0.01	2.11	0.19	0.10
	SD	5235	0.37	0.51	4.10	0.56	0.01	0.66	0.19	0.04
2015	Min	10	5.01	0.70	5.00	0.80	0.01	1.14	0.02	0.02
	Max	16,000	7.53	3.80	18.60	3.70	0.05	6.29	0.62	0.17
	Mean	4532	6.25	1.48	7.11	2.00	0.02	2.37	0.15	0.08
	SD	5007	0.45	0.50	3.99	0.52	0.01	0.73	0.10	0.03
2016	Min	10	5.77	0.70	5	0.80	0.01	0.93	0.02	0.04
	Max	16,000	7.03	2.80	14.30	3.90	0.05	4.63	0.66	0.19
	Mean	4432	6.31	1.34	7.95	1.91	0.02	2.17	0.17	0.09
	SD	4642	0.25	0.29	3.63	0.60	0.01	0.58	0.13	0.03
2017	Min	320	5.74	0.90	5	1.20	0.01	1.59	0.04	0.04
	Max	16,000	8.48	3.10	14.00	5.00	0.04	4.11	0.44	0.30
	Mean	3160	6.45	1.50	6.17	2.10	0.02	2.53	0.15	0.09
	SD	3196	0.38	0.39	2.33	0.66	0.01	0.45	0.09	0.04

Table 3. Chinese environmental quality standards for surface water (GB3838-2002).

	F. Coli CFU L^{-1}	DO mg L^{-1}	BOD_5 mg L^{-1}	COD_{Cr} mg L^{-1}	COD_{Mn} mg L^{-1}	Petroleum mg L^{-1}	TN mg L^{-1}	NH_3–N mg L^{-1}	TP mg L^{-1}
Class I [a]	200	7.50	3.00	15.00	2.00	0.05	0.20	0.15	0.02
Class II [b]	2000	6.00	3.00	15.00	4.00	0.05	0.50	0.50	0.10
Class III [c]	10,000	5.00	4.00	20.00	6.00	0.05	1.00	1.00	0.20
Class VI [d]	20,000	3.00	6.00	30.00	10.00	0.50	1.50	1.50	0.30
Class V [e]	40,000	2.00	10.00	40.00	15.00	1.00	2.00	2.00	0.40

[a] Class I standard is used for clean water that can be drunk after simple treatment (e.g., filtration) and sterilization. [b] Class II standard is used for slightly polluted water that can be drunk after routine treatment (e.g., flocculation, precipitation, filtration and sterilization). [c] Class III standard is used for centralized drinking water sources, fisheries, and swimming. [d] Class IV standard is used for industrial water and recreational water that are not directly contacted by human beings. [e] Class V standard is used for agricultural water and landscape water.

3.1.2. Nutrients

The monthly variation and a statistical summary of TN, NH_3–N and TP are shown in Figure 3 and Table 2, respectively. Generally, the flood/ebb tides did not affect the concentration of TN but slightly affected the concentration of NH_3–N and TP in the estuarine water. These nutrients showed a seasonal variation pattern (particularly clear for NH_3–N), with a decrease from spring to summer and an increase again in winter. This was primarily due to the dilution effect of rainfall (Figure 3) [33]. In summer (mainly July–August), heavy rainfall brought a large quantity of freshwater into the surface water, which led to lower concentrations of nutrients compared to other seasons.

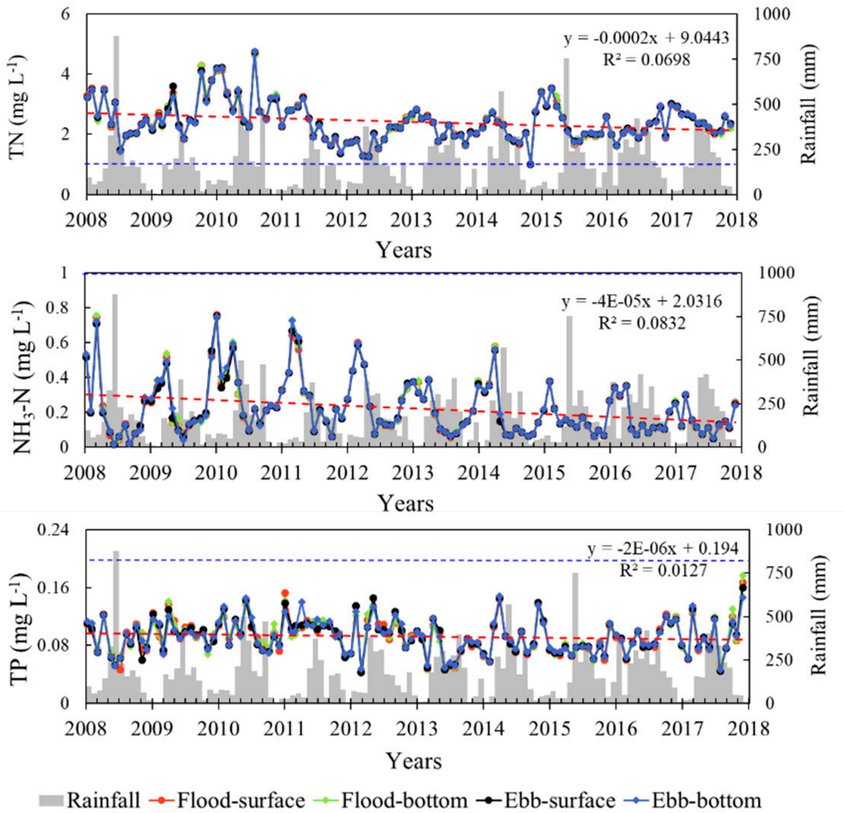

Figure 3. Temporal changes in total nitrogen (TN), ammonia nitrogen (NH_3–N), and total phosphorous (TP) in estuarine water measured from six sites (given as mean) in Nansha, Guangzhou, over the ten-year period (2008–2017). Rainfall data are presented as background information. The red dashed lines refer to the trendlines with equations and R^2 provided. The blue dashed lines refer to the Chinese environmental quality Class III standards for surface water.

The concentration of NH_3–N showed a declining trend over the last decade (Figure 3), and the annual mean concentration reduced from a maximum of 0.32 to 0.15 mg L^{-1} (Class II) (Table 2). In contrast, there was no significant reduction trend observed for TN and TP. From 2008 to 2017, the annual mean concentration of TN maintained at a high level (1.87–3.25 mg L^{-1}, Class V), and TP was quite stable from 2008 to 2017 (0.08–0.10 mg L^{-1}, Class II) (Table 2).

3.2. Distribution of Water Quality Parameters in Different Sampling Sites

The distribution patterns of F. Coli, DO, BOD_5, COD_{Cr}, COD_{Mn}, petroleum, TN, NH_3–N and TP in the six sampling sites were similar every year. The distribution of these water quality parameters in different sites over the last decade is summarized in Figures 4 and 5.

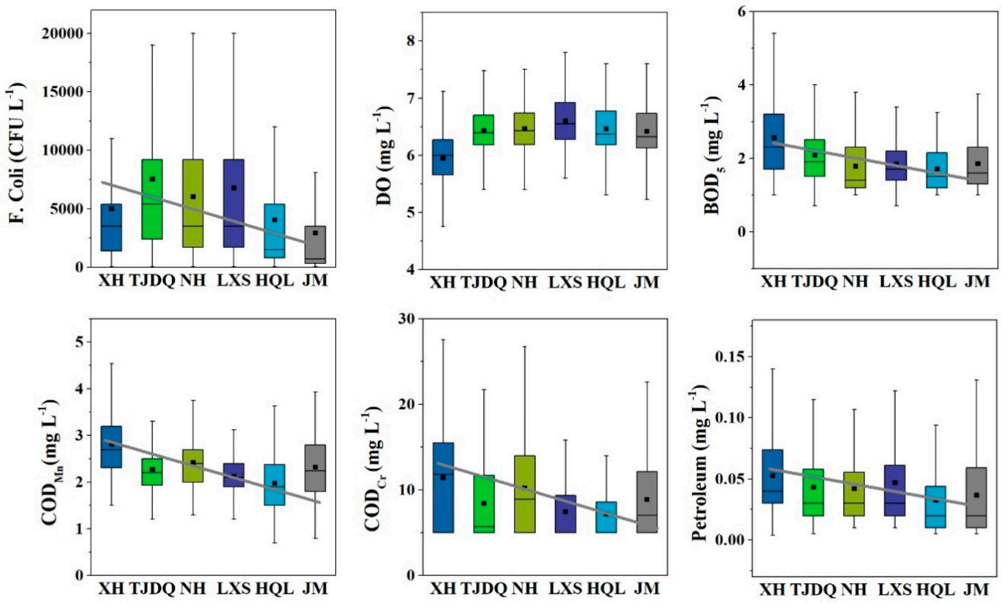

Figure 4. Concentration of F. Coli and physiochemical parameters (DO, BOD_5, COD_{Cr}, COD_{Mn} and petroleum) from six sites in Nansha, Guangzhou, from 2008 to 2017. The sampling sites are ranked according to their distance from the city center: XH < TJDQ < NH < LXS < HQL < JM. The boxes represent the 25th and 75th percentiles, and the whiskers represent the minimum and the maximum. The horizontal bars within boxes represent median. The black points inside boxes represent mean. All outliers are not shown.

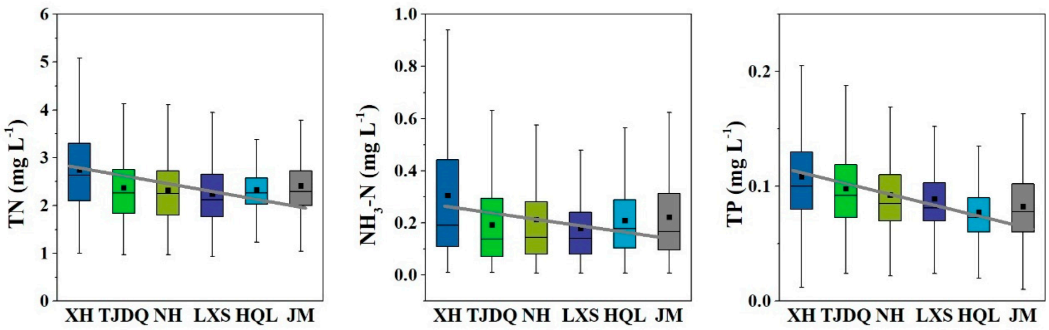

Figure 5. Concentration of nutrients (TN, NH_3–N and TP) in the estuarine water from six sites from 2008 to 2017 in Nansha, Guangzhou. The sampling sites are ranked according to their distance from the city center: XH < TJDQ < NH < LXS < HQL < JM. The boxes represent the 25th and 75th percentiles, and the whiskers represent the minimum and the maximum. The horizontal bars within boxes represent median. The black points inside boxes represent mean. All outliers are not shown.

In general, the concentrations of F. Coli, BOD_5, COD_{Cr}, COD_{Mn}, petroleum, TN, NH_3–N and TP showed a slight decreasing trend with increasing distance from the city center (Figures 4 and 5). Particularly, BOD_5, COD_{Cr}, COD_{Mn}, petroleum, TN, NH_3–N and TP were concentrated in the northernmost XH section from 2008 to 2017. The lower concentration of DO in the XH section compared to other sections over the last decade also supports the heavier pollution there (Figure 4). This was because the upper river runoff running through the urban area was an important source of various pollutants to the estuarine region. A previous investigation in the urban rivers of Guangzhou during 2006 to 2016 demonstrated that the mean concentrations of COD_{Cr} (42–1925 mg L^{-1}), BOD_5 (13–19 mg L^{-1}), TN (4.39–13 mg L^{-1}) and TP (0.39–1.1 mg L^{-1}) were much higher than the results obtained in this study (Table 2) [34–36]. The numerous industries and dense population distributed near the city center discharged industrial wastewater and domestic wastewater that was abundant in F. Coli, organic pollutants and nutrients. The XH site was the closest to the urban area compared to other sites, and it received a heavier loading of various pollutants compared to other sites. While upper river runoff plays a role as the major pollution source in the estuarine region, the concentration of pollutants in the interior is usually higher than that in the river mouth due to a dilution process [37,38].

In spite of the contribution of pollutants from the upper river, the local anthropogenic activities around sampling sites can serve as other sources for different pollutants. For example, the concentrations of F. Coli in the TJDQ, NH and LXS sections were higher than the XH section (Figure 4), because many local residents of Nansha lived near the TJDQ, NH and LXS sites, while few residents lived near the XH site. A high concentration of F. Coli can be discharged into nearby rivers from domestic wastewater and septic systems of local residents [39,40]. In terms of the southernmost JM section, the concentrations of BOD_5, COD_{Cr}, COD_{Mn}, TN, petroleum, NH_3–N and TP in the JM section were higher than expected. This was primarily due to the frequent shipping activities and aquaculture activities near the JM site. The Nansha port was situated to the east of the JM site, and shipping sewage brought additional BOD_5, COD_{Cr} and COD_{Mn} to the water [41]. Moreover, the shipping of petroleum products increased the concentration of petroleum in the JM section through operational ballasting activities and tank washing [42,43]. The aquaculture is distributed to the west of the JM site, and it brought additional TN, NH_3–N and TP to the water through the use of aquafeed and the discharge of aquatic animal wastes [44,45]. Consistent with our results, previous studies in estuarine water have demonstrated that pollutants can be derived from upper river runoff, regional activities, and adjacent seawater [46].

3.3. Water Quality Assessment

The water quality index is a unit-less number that expresses the overall quality of surface water by consideration of all monitored water variables. In other words, the WQI assessment system first transforms a set of measurements (chemical, physical and microbiological parameters) into a single number (0–100) and then classifies the water quality into several categories (poor to excellent). To comprehensively assess the water quality in this study, the popular CCME-WQI was calculated by using the different water variables obtained from the six sampling sites from 2008 to 2017 (Table 4).

Table 4. The water quality index and category from six sites from 2008 to 2017 created with the use of the Canadian Council of Ministers of the Environment Water Quality Index (CCME-WQI) model. P: poor (0–44), M: marginal (45–59), F: fair (60–79), G: good (80–94) and E: excellent (95–100). The sampling sites were ranked according to their distance from the city center: XH < TJDQ < NH < LXS < HQL < JM.

WQI	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
XH	54.8	72.2	52.1	56.7	76.0	82.9	83.8	82.2	88.6	84.0
TJDQ	66.5	80.4	72.8	75.3	77.0	84.3	83.7	82.5	83.3	84.6
NH	67.6	71.7	73.9	79.9	77.0	84.3	83.7	83.0	84.5	84.3
LXS	65.3	80.8	74.8	74.9	76.8	84.3	84.2	83.1	83.6	83.5
HQL	66.4	81.6	79.0	76.0	81.3	83.4	88.1	88.7	88.6	88.2
JM	68.8	80.7	63.0	80.0	83.1	88.4	88.2	88.9	88.8	87.8
Category	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**
XH	M	F	M	M	F	G	G	G	G	G
TJDQ	F	G	F	F	F	G	G	G	G	G
NH	F	F	F	F	F	G	G	G	G	G
LXS	F	G	F	F	F	G	G	G	G	G
HQL	F	G	F	F	G	G	G	G	G	G
JM	F	G	F	G	G	G	G	G	G	G

In different sampling sites, the CCME-WQI generally showed an increasing trend with increasing distance from the city center, indicating that the surface water quality in Guangzhou coastal water was primarily affected by the anthropogenic activities in the upstream city. The temporal variation, except in 2009, showed that the CCME-WQI in each sampling site increased gradually from 2008 (54.75–68.79) to 2017 (83.50–88.15). From 2008 to 2012, the water quality for most sampling sites belonged to the marginal–fair category. The major pollutants in the surface water from Nansha were TN, petroleum, and F. Coli. From 2013 to 2017, the water quality from all sampling sites was in the good category, and only TN continued to be a major pollutant (Figure 3). Collectively, these results suggested that the water quality in the Guangzhou coast has significantly improved during the last decade. However, more attention should be paid to the control and abatement of TN pollution in the watershed.

4. Discussion

Our study revealed that F. Coli was one of the major pollutants in the study area in 2008, with concentrations mostly exceeding the limit of the Class III standard (Figure 2 and Table 2). F. Coli in surface water can be derived from both human and animal feces [39,47]. In the highly urbanized city Guangzhou, the F. Coli primarily originated from domestic wastewater [48]. A rapid decrease in F. Coli was observed in October 2008 (Figure 2) due to the operation of the new Dashadi WWTP. This WWTP, with a wastewater treatment capacity of 20 t d^{-1}, serves 0.66 million persons, effectively solving the problem of fecal pollution in the Guangzhou estuary [49].

For the organic pollution parameters, BOD_5 showed a moderate-to-high correlation with COD_{Cr} (Spearman $\rho = 0.544$, $p < 0.01$) and COD_{Mn} (Spearman $\rho = 0.470$, $p < 0.01$) in terms of both temporal and site variation. These parameters were mainly affected by domestic and industrial wastewater [35]. The reduction of these parameters during the last decade could be attributed to strict local policy-making and multiple measures for pollution control and abatement. First, the sewage treatment system was greatly improved due to the construction of sewage collection pipe networks and wastewater treatment plants in Guangzhou from 2008 to 2017. The sewage collection pipe network increased from 1813 to 3762 km over the last decade [49]. The number of wastewater treatment plants doubled in 2010 in Guangzhou compared to 2009, and the domestic wastewater treatment rate reached 85% by 2010 (Figure 6b) [49]. In particular, this study showed that the BOD_5 and COD_{Cr} decreased rapidly in April 2010 (Figure 2), which corresponded with the running of many new wastewater treatment plants in mid-2010 in Guangzhou (Figure 6b) [49]. Second, the industrial wastewater discharge was well-controlled due to local industrial upgrading and environmental protection policies. As an important source for organic pollutants, the discharge of industrial wastewater in Guangzhou reduced remarkably from 34,475 t in 2008 to 20,605 t in 2017 (Figure 6a) [50]. In this study, industrial relocation could have been the major reason for the continuous reduction of COD_{Cr} from 2011 to 2012, as 100 factories were required to close or move from Guangzhou during 2010–2012 due to heavy pollution [20,51].

Petroleum was also a major pollutant in the estuarine water from 2008 to 2011. In the PRE, petroleum in water has mainly come from shipping vessels for oil transport and petroleum refinery effluents [43,52]. As shown in Figure 6c, the volume of freight (petroleum, natural gas and petroleum products) handled decreased from 30.6 to 25.4 million tons from 2008 to 2017, particularly in 2012 [50], corresponding to the large reduction of petroleum in the estuarine water in 2012 (Figure 2) that was recorded in this study. In addition, the production of oil products including gasoline, diesel oil and fuel oil in Guangzhou reduced gradually from 7.0 to 6.0 million tons during 2008–2017 [50], implying a decrease in the discharge of petroleum from refinery effluents.

In terms of the nutrients, TN was one major pollutant in the estuarine water throughout the entire decade, as the concentration of TN remained at a relatively stable level above the Class III limit (Figure 3). Nitrogen can be both derived from point sources (e.g., domestic and industrial wastewater) and non-point sources (e.g., agricultural wastewater and animal husbandry wastewater) [25,53,54]. In this study, TN was moderately correlated with BOD_5 (Spearman $\rho = 0.347$, $p < 0.01$), COD_{Cr} (Spearman $\rho = 0.358$, $p < 0.01$) and NH_3–N (Spearman $\rho = 0.358$, $p < 0.01$), implying the contribution from wastewater to TN levels. The high concentration of TN remaining in the estuarine water can be, on the one hand, due to the unsuccessful removal of TN in WWTPs. In China, nitrogen discharge from approximately half of WWTPs did not meet standards, probably due to operational overloading or the low carbon/nitrogen ratio of influents [55,56]. On the other hand, due to the use of nitrogen fertilizers in agricultural activities, the uncontrolled input of TN from farmlands could be another reason for the high concentration of TN in this study region. The annual consumption of chemical fertilizers (including nitrogenous fertilizers) was 252,097–311,751 t (Figure 6d) [50]. NH_3–N is a nitrogen form that is toxic to various aquatic organisms [57]. According to our study, the concentration of NH_3–N was within safe levels through the last decade and started to decrease, particularly from 2012 to 2017 (Figure 3). More study on nitrogen forms including organic nitrogen, NH_3–N, NO_3–N and NO_2–N is required to understand the transformation of NH_3–N in the estuarine water.

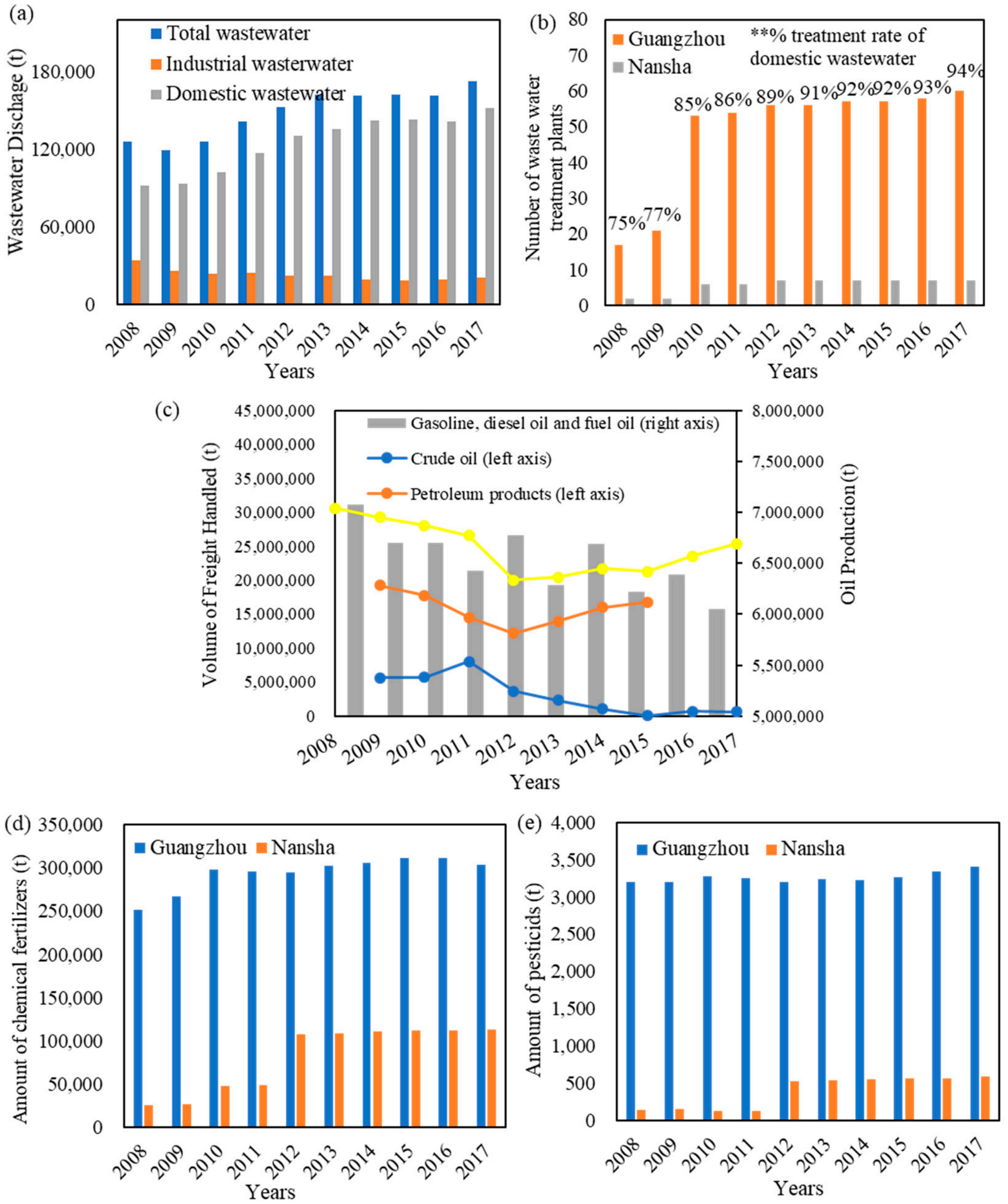

Figure 6. The situation of wastewater discharge (**a**), wastewater treatment plants (**b**), volume of oil freight handled and production (**c**), application of chemical fertilizers, (**d**) and usage of pesticides (**e**) in Guangzhou from 2008 to 2017 [49,50].

The concentration of TP was lower than the Class III limit and varied over a small range without a clear decreasing or increasing trend (Figure 3). TP showed no significant correlation ($p < 0.01$) with

BOD_5, COD_{Cr}, COD_{Mn} and TN, suggesting that wastewater was not the major source for TP. Because the sampling sites were surrounded by a large area of farmlands and phosphorus is often found in agricultural fertilizers and pesticides, TP can be released from non-point agricultural sources into estuarine water through surface runoff, subsurface flow and farm drainage [41]. Annual agricultural pesticide use (including organophosphorus pesticides) was 3203–3400 t in Guangzhou (Figure 6d,e) [50].

Collectively, with the decrease in the microbiological pollutant (F. Coli), organic pollution parameters (BOD_5, COD_{Cr} and COD_{Mn}) and the organic pollutant (petroleum), the overall water quality improved greatly from 2008 to 2017 in the estuarine water from south Guangzhou (Table 4). The reduction of pollutants can be attributed to local industrial upgrading, the installation of WWTPs, and the improvement of sewage collection systems. However, TN still remained the major pollutant affecting the water quality in the Guangzhou estuarine water over the latter half of the study period (2012–2017) (Figure 3 and Table 4). Similarly, a five-year (2008–2013) study reported the improved control of F. Coli, COD_{Mn}, and BOD_5 but the deterioration of TN and TP in the Three Gorges Reservoir, China [41]. In addition, a previous study in Korea also demonstrated that similar pollution control measures during 2005–2010 were effective for decreasing the land-based loads of COD and suspended sediment (SS), ultimately lowering the pollution level in Masan Bay, whereas the TN and TP were not controlled due to the large inputs from non-point sources [33]. Therefore, the reduction of nutrient inputs (including TN and TP) remains a challenge to a wide range of anthropogenically-influenced watersheds. In our study area, the inputs of TN to estuaries can be controlled through two pathways. First, for control point sources, the introduction of enhanced nitrogen removal techniques in Guangzhou wastewater treatment plants is urgently required. Advanced process controls and new biological treatment processes can be applied to upgrade the current WWTPs, including the modified anaerobic–anoxic–oxic (AAO) process, the membrane bioreactor and annamox technology. Second, for control non-point pollution sources, improved management plans are required for water and fertilizers in farmlands.

5. Conclusions

The present study analyzed the continual variation of F. Coli, physiochemical parameters, and nutrients from 2008 to 2017 in the estuarine water from south Guangzhou. Overall, F. Coli, BOD_5, COD_{Cr}, COD_{Mn}, petroleum and NH_3–N in water showed a clear decreasing trend, while TN and TP varied in a relatively stable range over the last decade. The biochemical pollutants and nutrients in the estuarine water most likely originated from the upper river due to the wastewater discharge, fecal pollution, and agricultural input. The overall water quality was improved from the marginal–fair level to the good level, particularly after 2012. However, TN remained a major pollutant in the estuarine water over the study period. The successful management of F. Coli, BOD_5, COD_{Cr}, COD_{Mn} and petroleum could be attributed to industrial relocation, upgrading, and improvement of sewage treatment systems. The removal of TN from point and non-point sources remains a significant challenge. Enhanced TN treatment techniques should be implemented in the future upgrading of WWTPs in Guangzhou, and the improved management of water and fertilizers is required. In summary, this research shows the influence of pollution control measures on estuarine system improvement and will be useful to policy-makers in search of pathways to balance economic development with environmental protection.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/12/1/59/s1, Table S1: The storage condition, container, and time for water samples. Table S2: Correlation coefficient matrix for different water quality parameters in Nansha, Guangzhou (2008–2017).

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