

Xueping WANG^{1*}, Huibin ZHU¹, Yue GENG¹, Kexuan DING¹ and Linan YE^{2*}

INVESTIGATION THE EFFECT OF THE MAIN LAND-BASED POLLUTANTS IN XIANGSHAN BAY

Abstract: This paper analyses and discusses the monthly and annual changes of chemical oxygen demand (COD), total nitrogen (TN), and total phosphorus (TP) concentrations from main sewage discharge ports in Xiangshan Bay. Using monitoring data obtained from 2010 to 2019, it systematically examines the monthly variation characteristics of the sewage discharge ports and the interannual changes in the fluxes of major pollutants into the sea. The concentrations of COD, TN, and TP, which were relatively high in November and January-March, generally declined. The annual and monthly changes fluctuated, but the flux into the sea generally decreased. The ecological environment of the nearby sea area is adversely affected, chiefly by land-based pollutants. During the five-year period, COD mainly came from soil erosion and domestic pollution, while TN and TP mainly came from agricultural activities and soil erosion. Hence, it is both necessary and urgent to improve the management of the sewage outfalls from land sources into the sea.

Keywords: Xiangshan Bay, interannual variation, monthly variation, flux into the sea, land-based pollution, ecological environment

Introduction

Xiangshan Bay has a natural environment characterised by abundant aquatic resources, including economic aquatic resources, and diverse ecological types [1]. It is known as the national “large fishing pond” and is a rare and protective land resource. Xiangshan Bay, Ninghai, Fenghua, Beilun, Yinzhou, and five districts along the coast of Xiangshan Bay have 95 small and large streams and an average annual runoff of $12.89 \times 10^8 \text{ m}^3$ [2]. A semi-closed bay, Xiangshan Bay is a relatively independent and fragile ecosystem. Semi-closed bays are susceptible to environmental pollution and ecological damage from land-based sources [3]. The development of the marine economy has intensified human activities [4-6], causing various environmental problems in offshore harbours that have become increasingly serious [7]. By understanding changes in the estuary environment and their ecological impact [8-10], proper regulation, sustainable use, and reasonable development of Coastal areas Marine ecosystems can be achieved [11, 12].

Owing to the rapid development of the coastal economy of Xiangshan Bay in recent years, the contradiction between protecting the marine environment and increasing economic growth has become increasingly prominent [13, 14]. Governments at all levels

¹ Yellow River Conservancy Technical Institute, 475004, Henan, China, ORCID: XW 0000-0003-2851-521X, HZ 0000-0003-2427-3372, YG 0000-0001-8081-5952, KD 0000-0003-3194-0743.

² Ningbo Marine Environment Monitoring Center, Ningbo 315100, Zhejiang, China, ORCID: LY 0000-0001-7852-8903.

* Corresponding authors: wxpzky@163.com; yelinan2018@163.com

have attached great importance to the sustainable development of the Xiangshan Bay area. Total discharge control targets are being monitored to ensure the normal ecological function of both Xiangshan Bay and the adjacent sea area. Studies investigating and evaluating the relevant sea areas near Xiangshan Bay are abundant [15-20], while those examining the water quality and pollutant fluxes of the sewage discharge ports along the coast are limited. Using water quality survey data of Xiangshan Bay from 2007 to 2015, Wu et al. found that the nitrogen and phosphorus sources on land mainly come from nitrogen fertiliser, phosphate fertiliser, and livestock waste [21]. Evaluating the water quality in the aquaculture area in the target mountain port, Zhao concluded that inorganic nitrogen, active phosphate, and petroleum are the main factors affecting the aquaculture area [22]. Wang et al. analysed ecological factors, such as chlorophyll a, water temperature, water body, and sediments, at 22 stations in the Xiangshan Bay Marine Ranch planning area, and found that fish reefs increase the level of primary productivity in this sea area [19]. The evaluation results of Xu et al. [23], who combined with the actual situation of Xiangshan Bay to reconstruct a new pressure-state-response model, can better reflect the eutrophication pressure and symptom level of Xiangshan Bay.

Considering the vital role of Xiangshan Bay in Ningbo's marine economy, as well as the current environmental problems in the sea area, it is necessary to regularly monitor the water quality and pollution status in the estuary. This would help achieve the sustainable development and use of marine resources in the target mountain port. Using monitoring data obtained from 2010 to 2019, this paper systematically examines the monthly variation characteristics of the sewage discharge ports and the interannual changes in the fluxes of major pollutants into the sea. The land source input of Xiangshan Bay serves as a reference for changes in water quality, total control of pollutants entering the sea, and scientific planning for sea use. It also provides relevant marine ecological and environmental management departments a basis for decision-making.

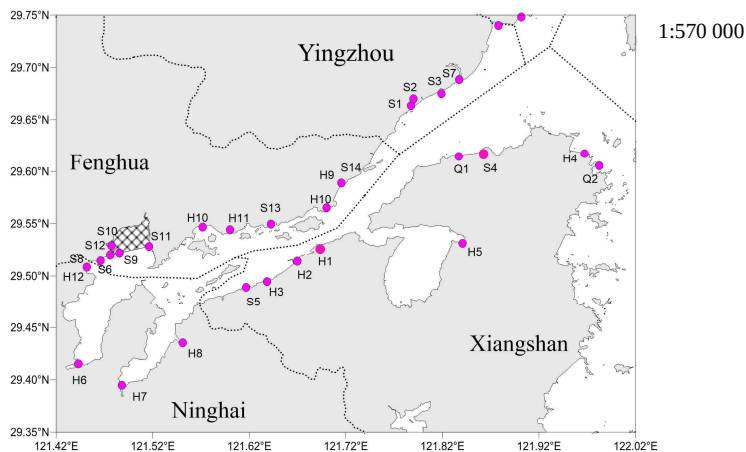


Fig. 1. Sampling sites

The study used survey data on the concentration of main pollutants in the estuary from the Marine Environmental Bulletin of Ningbo. A total of 28 monitoring stations were arranged at the survey site, including 12 rivers, 14 sluice stations, and two direct discharge

outlets of enterprises. Figure 1 shows the distribution of monitoring stations at the survey site.

Materials and methods

Sampling stations

This study is based on the monitoring survey data of the concentration of main pollutants in Xiangshan Bay from 2010-2019 Ningbo Marine Environmental Bulletin. A total of 28 survey sites are arranged at the survey site, the specific distribution is shown in Figure 1, includes 12 rivers, 14 sluice stations and 2 direct discharge outlets of enterprises are arranged in the survey station.

Sampling and analysis

The water samples were collected and transported according to the following marine environmental assessment standards: Technical Regulations for the Monitoring of Total Pollutants into the Sea [24]; Ocean Monitoring Specifications, Part 3: Sample Collection [25], and Marine Monitoring Code, Part 4: Seawater Analysis [26]. Based on Ye et al. [1], as well as other major pollution factors that affect the water quality of the target port, chemical oxygen demand (COD), total nitrogen (TN), and total phosphorus (TP) were identified as the major land-based pollutants to be analysed. Table 1 shows the method for analysing data.

Table 1

Sample analysis method of the elements in water

Project	COD	TN	TP
Analysis method	Dichromate method	Alkaline potassium persulfate digestion UV spectrophotometry	Ammonium molybdate spectrophotometry
Method source	GB 11914-1989	GB 11894-1989	GB 11893-1989

Data processing and analysis

Evaluation criteria

Rivers and sluices adopt the China Surface Water Environmental Quality Standards [27], and industrial enterprises directly implement the standards that correspond to the type of enterprise. Printing and dyeing enterprises adopt the Class I standards of the Discharge Standards of Water Pollutants for Dyeing and Finishing of Textile Industry. Table 2 shows the specific classification values.

Table 2

Environmental quality classification standards for major pollutants [mg/L]

Number	Standards	Project		Class I	Class II	Class III	Class IV	Class V
1	Water quality standards	COD	≤	15	15	20	30	40
2		TP	≤	0.02	0.1	0.2	0.3	0.4
3		TN	≤	0.2	0.5	1.0	1.5	2.0
4	Environmental quality standards for printing and dyeing enterprises	COD	≤	100	180	500	-	-

Calculation of flux into the sea

To calculate the flux of major pollutants into the sea, the average concentration and runoff of pollutants entering the sea during the corresponding period was determined. The amount of pollutants entering the sea was estimated according to formula:

$$W = \sum_{i=1}^m M_i \times Q_i \quad (1)$$

where W is the total amount of pollutants entering the sea; M_i is the average concentration of pollutants entering the sea; Q_i is the runoff into the sea; and m is the number of days in the month.

Results and discussion

Annual change characteristics of pollutants

Figures 2-4 shows the annual changes in the concentrations of major pollutants based on the sum of the average monthly monitoring values of COD, TN, and TP in Xiangshan Bay from 2010 to 2019. The highest sum of the monthly average COD concentration of each estuary, which was 1,238.2 mg/L, was recorded in 2015. There was a steady decline from 2016 to 2018. By 2019, it decreased to 1,026.2 mg/L, which is 17.1 % lower than the value recorded in 2015. The highest sum of the annual average TN and TP concentration in Xiangshan Bay, which was 95.41 and 2.947 mg/L, respectively, was also recorded in 2015. TN declined, and its decrease from 2016 to 2019 was more obvious. TP increased slightly in 2018 but decreased on the whole. By 2019, the TN and TP concentration dropped to the minimum value, which was 57.13 and 1.890 mg/L, respectively. The values were 40.1 and 35.9 % lower than the values recorded in 2015.

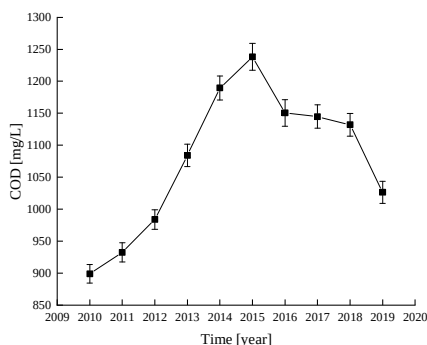


Fig. 2. COD concentration into the Xiangshan Bay for the period from 2010 to 2019

In terms of the total annual sea entry volume, COD, TN, and TP in Xiangshan Bay significantly declined during the five-year period, with the highest values recorded in 2015. According to Wu et al. [21], significant eutrophication occurred in the estuary from 2007 to 2015, which began to increase in 2015. From this, it can be surmised that the water quality of the sea area adjacent to Xiangshan Bay was largely affected by land-based pollutants in 2015. The carried N and P mainly come from domestic, industrial enterprise, and aquaculture pollution distributed near the river basin [28]. Domestic sewage is higher in

land-based pollutants, comprising higher amounts of COD, nitrogen, phosphorus, while the content of heavy metals is relatively few [29]. The N and P content accounted for more than 80 % of all land-based pollutants.

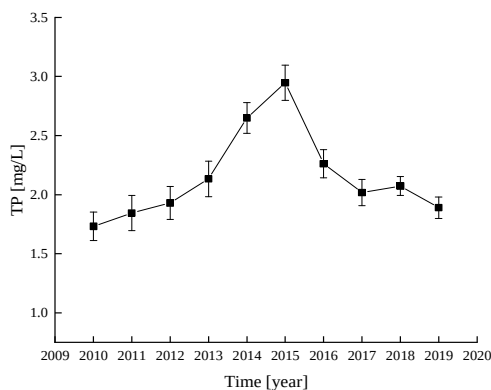


Fig. 3. TP concentration into the Xiangshan Bay for the period from 2010 to 2019

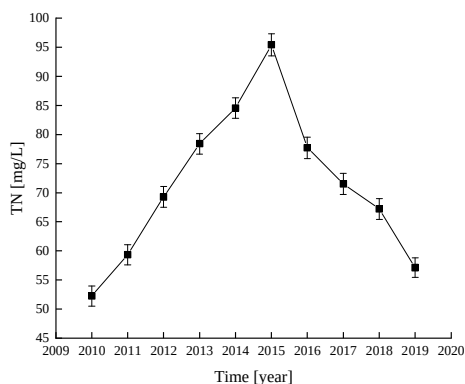


Fig. 4. TN concentration into the Xiangshan Bay for the period from 2010 to 2019

Characteristics of monthly changes of pollutants

To examine the monthly changes of COD, TN, and TP concentrations, the minimum, maximum, and average values of the 2016 monthly monitoring data were used. Figures 5-7 and Table 3 show the changes determined from the analysis. The COD concentration of pollutants entering the sea through Xiangshan Bay was 9.5-674 mg/L from January to December, while the average value was 54.2-134.9 mg/L. From this, it can be gleaned that the overall monthly average belongs to inferior V water quality. The TN concentration range from January to December was 1.84-48.90 mg/L, while the average range was 4.67-7.48 mg/L. All enter the sea with inferior V water quality. The TP concentration range was 0.027-1.350 mg/L from January to December, while the average value was 0.165-0.239 mg/L, of which the average value from April to December belonged to III water quality. In March, it entered the coastal waters of Xiangshan Bay with Class IV water

quality. From the perspective of monthly fluctuations, the fluctuation of the maximum COD was more obvious, indicating that the monthly pollution in some of the survey sites had changed significantly.

Table 3

Content range and mean value of monthly variation of main pollutants in 2016 [mg/L]

Month	COD		TN		TP	
	Range	Mean value	Range	Mean value	Range	Mean value
January	26.3-451.0	110.0	3.99-22.24	6.49	0.056-0.747	0.205
February	26.8-481.3	108.4	1.84-9.47	4.67	0.027-1.350	0.224
March	21.5-536.0	127.3	2.87-48.90	6.93	0.037-0.888	0.239
April	13.9-298.0	93.9	2.36-11.80	5.28	0.042-0.648	0.173
May	21.0-654.0	87.8	3.44-16.60	6.05	0.039-0.706	0.165
June	25.0-440.1	77.4	4.34-13.29	7.11	0.053-0.660	0.165
July	12.6-674.0	132.9	4.53-13.67	7.48	0.049-0.743	0.182
August	17.6-610.0	95.6	4.43-15.70	6.87	0.064-0.786	0.185
September	14.5-350.0	91.1	3.78-18.40	6.75	0.061-0.306	0.178
October	20.9-304.0	54.2	4.54-13.70	6.96	0.065-0.684	0.183
November	9.5-358.0	78.4	4.64-14.01	7.48	0.072-0.394	0.198
December	12.2-360.5	93.3	3.43-10.55	5.65	0.060-0.613	0.165

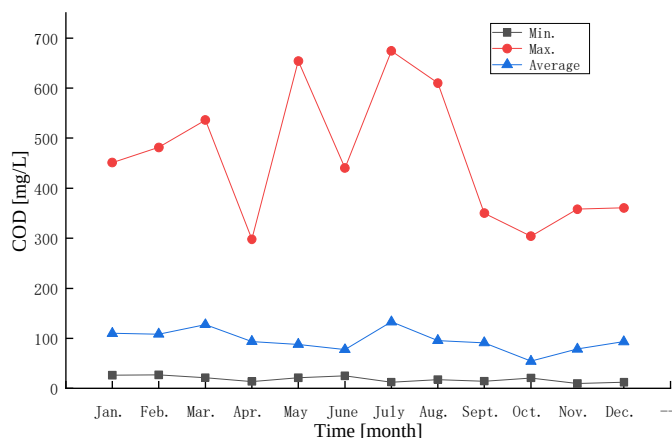


Fig. 5. Monthly variation of COD concentration in Xiangshan Bay

The averages in January, February, March, and July were the highest, while the average in October was the lowest. The COD values of the survey sites Q1, Q2, Q3, and Q4 were relatively high. COD mainly resulted from human activities, such as industrial enterprise pollution and domestic pollution, as well as the impact of precipitation on the day of monitoring and sampling. The fluctuation of the maximum value of TN was also relatively obvious, indicating that the monthly pollution in some of the survey sites had changed significantly. The averages in June, July, and November were the highest, while the average in February was the lowest. The highest TN value was recorded in the survey sites Q4 and S12. Similarly, the fluctuation of the maximum value of TP was also more obvious, indicating that the monthly pollution in some of the survey sites had changed

significantly. The averages in January, February, March, and November were the highest, while the averages in May, June, and December were the lowest. The highest TP value was recorded in the survey sites Q1 and S12.

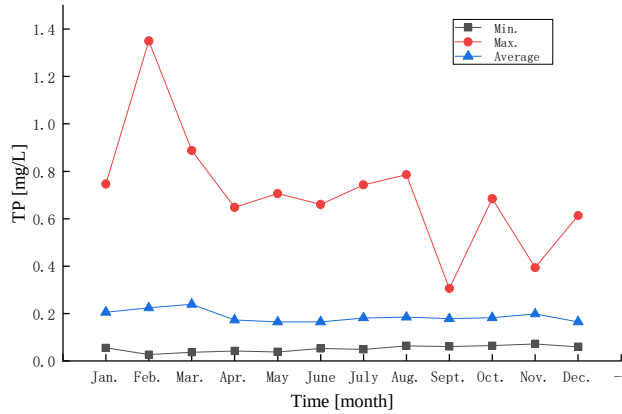


Fig. 6. Monthly variation of TP concentration in Xiangshan Bay

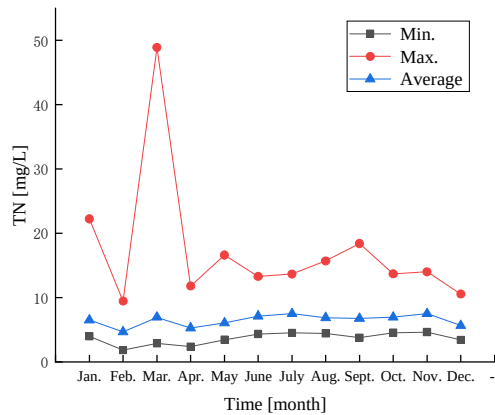


Fig. 7. Monthly variation of TN concentration in Xiangshan Bay

From the above analysis, it can be inferred that COD, TN, and TP values in Xiangshan Bay were relatively high in November and January-March, and mainly concentrated near the bottom of the port and into the sea. Analysing the water quality at the port of Shanshan Bay, Yang et al. found that the maximum phosphate concentration was at the bottom of the port [30]. By analysing the nitrate nitrogen and oxygen isotopes, confirmed that there were mores sources of N at the bottom of the port of Xiangshan Bay. It also explains why the N and P concentrations at the bottom of the port of Xiangshan Bay were higher than those in the port.

Estimation and source analysis of pollutant flux into the sea

Estimation of pollutant flux into the sea

Based on the monitoring results of the water quality COD, TN, and TP of 26 survey sites in the surrounding waters of Xiangshan Bay, the influx and flow of major river pollutants into the sea were calculated using Formula (1) total flux.

(1) The flux of major pollutants into the sea-river

Table 4 shows the calculation results of the monitoring data of 12 rivers in Xiangshan Bay in 2014. The total COD flux into the sea was 9,027.35 t (t = tonne = 10^6 g = 10 Mg). Yangong River contributed the most at 341.18 t, accounting for 37.8 %, followed by Tamkang River, Sunken River, Fuxi River, and Qiancang River. The COD that entered into the sea from these five rivers accounted for 88.1 % of the total COD flux. The TN flux into the sea was 562.22 t. Yangong River contributed the most at 135.18 t, accounting for 24 %, followed by Zhuhu River and Dangang River. The TN inflows of these three rivers accounted for 60.4 % of the total TN inflows of the rivers. The TP flux into the sea was 77.36 t. Yangong River contributed the most at 35.02 t per year, accounting for 45.3 %, followed by Tamkang River and Qiancang River. The TP flux into the sea of these three rivers accounted for 66.6 % of the total phosphorus flux into the sea.

Table 4

Main river pollutant flux to the sea

Codes	Name of river	Flow [m ³ /a]	COD [t/a]	TN [t/a]	TP [t/a]
H1	Danchang River	56764800	1237.47	91.220	8.360
H2	Xizhougang River	17029440	204.35	13.380	1.830
H3	Xiashenggang River	24282720	1307.62	37.750	7.510
H4	Qiancang River	21444480	933.91	53.880	8.170
H5	Yalinxi River	8703936	239.36	16.630	1.440
H6	Tuxi River	23652000	1066.71	36.070	1.680
H7	Yangong River	59130000	3411.80	135.080	35.020
H8	Dajia River	3311280	na	5.410	0.500
H9	Songao River	1513728	12.56	3.520	0.370
H10	Chunhu River	37843200	556.30	113.340	6.040
H11	Qiucun River	17376336	na	46.550	4.800
H12	Xiacheng River	3460288	57.27	9.390	1.640
Total			9027.35	562.22	77.36

na = data unavailable

(2) The flux of major pollutants into the sea-sluice

Table 5 shows the calculation results of the monitoring data of pollutants entering the sea through 14 sluices in Xiangshan Bay in 2014. The COD flux into the sea was 286.80 t. Hongsheng Haitang No. 1 sluice contributed the most at 79.44 t, accounting for 27.7 %, followed by Dasongjiang sluice and Hongsheng Haitang sluice 3. The COD influx of these three sluices accounted for 34.5 % of the sluice COD influx. The TN flux into the sea was 258.44 t. Sanshan Gate contributed the most at 103.87 t, accounting for 91 % of the TN sluice flux of the sluice gate, and the rest were relatively low. The TP flux into the sea was 7.23 t. Sanshan Gate contributed the most at 0.415 t, accounting for 25.1 %, followed by Hengjiang Gate. The TP flux into the sea of these two sluices accounted for 41 % of the total phosphorus flux into the sluice.

Table 5

Pollutant flux into the sea of each sluice

Codes	Name of sluice	Flow [m ³ /a]	COD [t/a]	TN [t/a]	TP [t/a]
S1	Hengshan sluice	105.9	4.99	0.300	0.075
S2	Xiaking sluice	707.7	na	1.159	0.138
S3	Dashongjiang sluice	320.0	25.15	0.659	0.186
S4	Mouse mountain sluice of Xianxiang River	41.0	3.48	0.085	0.031
S5	Paitou village sluice	27.6	2.58	0.154	0.055
S6	Cuijia sluice	27.6	5.25	0.497	0.030
S7	Sanshan sluice	234.5	7.96	103.870	0.415
S8	Feijia sluice	91.9	na	0.248	0.044
S9	Hongsheng Haitang 2 sluice	72.5	7.75	0.574	0.024
S10	Hongsheng Haitang 3 sluice	134.9	23.17	0.368	0.022
S11	Hongsheng Haitang 1 sluice	331.2	37.06	1.762	0.133
S12	Feiyue sluice	86.8	16.55	2.033	0.052
S13	Hengjiang sluice	214.8	na	1.650	0.263
S14	Shizikou sluice	244.0	na	0.796	0.187
Total			133.94	114.16	1.655

na = data unavailable

(3) The flux of major pollutants into the sea-the enterprise's direct discharge

Table 6 shows the calculation results of the flux of major pollutants into the sea. The calculations were based on the monitoring data of the pollutant concentration at the direct outlets of two enterprises in Xiangshan Bay in 2014, using the wastewater discharge value for the same year. The flux of COD into the sea was 80.38 t. Ningbo Sanyou Printing and Dyeing Co., Ltd. contributed the most at 65.67 t, accounting for 81.7 % of the COD flux of the company's direct outlet, while Xiangshan Xinguang Knitting and Dyeing Co., Ltd. accounted for 18.3 %. The TN flux into the sea was 5.84 t per year. Ningbo Sanyou Printing and Dyeing Co., Ltd. contributed slightly at 3.39 t, accounting for 58.0 % of the industrial direct discharge TN flux into the sea. The TP flux into the sea was 0.35 t per year. Ningbo Sanyou Printing and Dyeing Co., Ltd. contributed significantly at 0.314 t, accounting for 89.7 % of the TP flux into the sea at the industrial outlet, while Xiangshan Xinguang Knitting and Dyeing Co., Ltd. accounted for 10.3 %.

Table 6

Pollutant flux into the sea at the direct outlet of enterprises

Codes	Name of straight outlet	Flow [m ³ /a]	COD [t/a]	TN [t/a]	TP [t/a]
Q1	Sanyou Dyeing and Printing Company	730,000	65.70	3.390	0.350
Q2	Xinguang Knitting Company	730,000	14.68	2.450	0.040
Total			80.38	5.840	0.390

Spatial distribution of pollutant flux into the sea

According to the analysis of the effective spatial heterogeneity in the sea area near Xiangshan Bay, Xiangshan Bay is roughly divided into five areas (A, B, C, D, and E) from the port to the bottom of the port [31]. In 2016, the average monthly concentrations of COD, TN, and TP monitored at 28 survey sites were used to calculate the sea fluxes. Table 7 shows the calculation results of COD, TN, and TP fluxes into the sea. The COD flux into

the sea contributed the most land-based pollutants to Area D at 2,318.47 t, and to Area E at 2,172.78 t, together accounting for 55.9 % of the total land-based pollutants recorded at the survey sites. Area B and Area A received the least amount of land-based pollutants, accounting for 29.1 %. The TN flux into the sea contributed the most land-based pollutants to Area E at 998.63 t, and to Area D at 742.26 t, together accounting for 53.9 % of the total land-based pollutants at the survey sites. Area B and Area A received the least amount of land-based pollutants, accounting for 28.7 %. The TP flux into the sea contributed the most land-based pollutants to Area E at 208.05 t, and to Area D sea area at 154.64 t, together accounting for 53.9 % of the total land-based pollutants at the survey sites. Area B and Area A received the least amount of land-based pollutants, accounting for 28.7 %.

Taken together, COD, TN, and TP were mainly concentrated in Area D and Area E, and least present in Area B. Tables 4-6 show that in 2014, COD was 9,241.67 t, TN was 682.22 t, and TP was 79.41 t. In comparison, in 2016, the COD, TN, and TP fluxes of Xiangshan Bay decreased slightly by 13.2, 1.4, and 7 %, respectively. Also, from 2010 to 2019, the major pollutants in the Xiangshan Bay Land Source Pollution Monitoring Station, as well as the monthly changes, fluctuated. However, the overall flux of COD, TN, and TP into the sea declined, reducing ecological and environmental pressure in the Xiangshan Bay area in Hong Kong [32]. This is closely related to the efforts of the Ningbo Municipal Government, which has been actively promoting pollution reduction in the past few years. Hence, based on these findings, efforts to reduce emissions should be continued, focusing on adjusting the industrial structure and optimising the spatial layout of source strength.

Table 7

Content range and mean value of monthly variation of main pollutants in 2016

Sea area	COD [mg/L]	TN [mg/L]	TP [mg/L]
A	1180.49	96.84	10.37
B	1161.00	96.45	10.02
C	1197.29	116.93	12.65
D	2318.47	154.64	18.61
E	2172.78	208.05	22.25
Total	8030.04	672.90	73.89

Source analysis of main pollutants entering the sea

Table 8 shows the main sources of COD, TN, and TP in Xiangshan Bay in 2016, classified and summarised by industry, life, livestock and poultry, fertiliser, and soil erosion. The land-based pollution sources of COD in Xiangshan Bay were mainly water and soil erosion and domestic pollution, together accounting for 84.86 % of the total. The land-based pollution sources of TN were mainly agriculture and water and soil erosion, together accounting for 86.85 % of the total. They are mainly agriculture and soil erosion, which together account for 80.51 % of the total; industrial pollution sources account for a relatively small proportion, accounting for about 8.77 % of the total COD and 1.19% of the total TN. COD mainly came from soil erosion and domestic pollution, while TN and TP mainly came from agricultural activities and soil erosion. Therefore, it is particularly important to conduct further research on the estimation and control of N and P emissions from non-point sources in small watersheds.

Table 8

Main sources of pollution in Xiangshan Bay

Types of land-based pollution	COD [mg/L]		TN [mg/L]		TP [mg/L]	
	Strong source [t/a]	Proportion [%]	Strong source [t/a]	Proportion [%]	Strong source [t/a]	Proportion [%]
Industry	541.91	8.77	32.12	1.19	na	na
Life	2,378.54	38.51	147.34	5.47	22.58	7.64
Livestock	393.45	6.37	174.59	6.49	35.01	11.84
Agriculture	na	na	1,758.01	65.31	134.13	45.38
Soil erosion	2,863.04	46.35	579.55	21.53	103.84	35.13
Total	6,176.95	na	2,691.59	na	295.55	na

na = data unavailable

Conclusion

From 2010 to 2019, the concentrations of COD, TN, and TP in Xiangshan Bay generally declined. The values were relatively high in November and January-March, and mainly concentrated in the estuary near the bottom of the port, particularly Area D and Area E. The most serious eutrophication occurred in 2015. The annual and monthly changes fluctuated, but the flux into the sea generally decreased. The ecological environment of the nearby sea area, particularly its water quality, is largely affected by land-based pollutants. During the five-year period, COD mainly came from soil erosion and domestic pollution, while TN and TP mainly came from agricultural activities and soil erosion. The survey data can be used to determine the bio-ecological indicators of the sea area near the sewage outfall, namely, the diversity, density, and biomass of benthic organisms. Taking Yangong River in Ninghai County as an example, the analysis shows that land-based pollutants adversely affect the ecological environment of the estuary and its adjacent sea area. The overall ecological environmental impact tends to change in a good direction. Hence, it is recommended that the management of land-based sewage outfalls be improved and strengthened.

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