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Review article

Monitoring and discussion on river carbon and nitrogen fluxes in the Pearl River Estuary region

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ABSTRACT

Rivers link land and sea, playing an important role in the global carbon and nitrogen cycles. By conducting surveys and research on river flow in a specific region, we can gain a better understanding of the nitrogen and carbon sinks in the area and their contributions to the environment. In this study, we conducted bi-annual sampling and monitoring of river flow in the Pearl River Delta downstream of Zhuhai, China, and collected hydrological information. The results show that the total flow in the dry season (939.22 m^3/s) is lower than that in the rainy season (1556.40 m^3/s); the highest concentration of total organic carbon is in the dry season (14.70 mg/L) and the lowest is in the rainy season (10.95 mg/L); the total organic carbon emission flux is lower in the dry season (1804.45 g/s) than in the rainy season (3331.04 g/s), and the maximum emission points in both seasons are at the Damenkou Waterway, with values of 2327.60 g/s and 917.87 g/s, respectively; the highest concentration of total nitrogen is in the dry season (40.20 mg/L) and the lowest is in the rainy season (17.80 mg/L); the total nitrogen flux is lower in the dry season (2204.68 g/s) than in the rainy season (2403.47 g/s). Inorganic nitrogen is the main component of total nitrogen, and ammonium nitrogen is the main component of inorganic nitrogen. The maximum flux of total nitrogen at both sampling frequencies is in the main entrance waterway. Same as the maximum flux point of carbon emissions, the main reason is that this point has the highest flow rate in this survey, which further proves that it is the river that needs the most attention for pollution control. By referring to historical statistical data and combining it with the results of this survey, we can provide data support for the next phase of pollution control in surrounding waters.

1. Introduction

The carbon and nitrogen reservoirs in the Earth system mainly include the atmosphere, ocean, terrestrial ecosystems, and the lithosphere. The lithosphere reservoir has a circulation cycle on a geological timescale, so carbon and nitrogen cycle research refers to the flow of elements between the three main storage reservoirs in the terrestrial, marine, and atmospheric ecosystem. River transport is an important part of the global cycle, and it plays a binding role in the circulation processes of terrestrial and marine ecosystems [1]. As a major channel from land to ocean and the atmosphere, it is an important part of the water ecosystem and plays a crucial role in the

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carbon balance of ecosystem. It has a crucial impact on the photopermeability, secondary production, and nitrogen dynamic processes in the aquatic system, and helps to emit carbon dioxide to the atmosphere, transport metals and organic trace pollutants, and provides energy and nutrient sources for many aquatic organism.

Natural cycles occur spontaneously and remain in a balanced state for a long period of time. However, human activities have disrupted this balance in a very short period of time. Especially since the industrial revolution in the 18th century, modern industries and agriculture have developed rapidly, and human activities have had a growing impact on the water environment, leading to an increasing number of rivers being polluted to varying degrees by industrial waste discharge, agricultural fertilizers, atmospheric deposition, aquaculture, etc [2–5]. Land-based inputs have led to an increase in nitrogen concentrations, causing eutrophication of lake and reservoir waters and deterioration of nearshore marine waters and harmful algal bloom. Large amounts of algae growth lead to deterioration of water quality, disruption of ecological balance, and the death of fish, poultry, and waterbirds, and even direct harm to human life [6–10]. This affects human production and life, hinders the smooth development of global society and economy, and water total nitrogen is closely related to the water environment level and is an important indicator of water environment quality [11–13].

The Pearl River Delta (PRD) is a leading region for rapid economic development since the reform and opening-up, and its internal environmental pollution problems have always been the focus of attention. Due to its high population density and high concentration of industrialization, as well as the fact that the Pearl River Delta is located in the typical subtropical monsoon climate zone, with a flat internal terrain and a well-developed water system, pollutants can quickly disperse and cause ecological damage or even pollute the South China Sea area [14–20]. According to the recent release of the China Marine Ecological Environment Status Bulletin, the Pearl River Estuary is still one of the most polluted coastal areas in China. Controlling the total amount of pollutants entering the sea is the top priority for improving the ecological environment quality in the Pearl River Estuary. The "Fifth Five-Year Plan for Marine Ecological Environmental Protection" has clearly defined the responsibilities of coastal cities and upstream provinces for the management of rivers that flow into the sea. It also calls for targeted expansion of the total nitrogen and other pollutants discharge control area. Total discharge control is an important means of promoting pollution reduction and improving marine environmental quality. It has great significance for solving marine environmental problems, achieving overall improvement in marine ecological environment quality, and promoting sustainable economic and social development.The objectives in this study are to preliminarily understand the carbon and nitrogen flux and pollution status of the Pearl River Estuary region through seasonal sampling and monitoring of inland rivers flowing into the ocean in Zhuhai City, and provide data support for subsequent research.

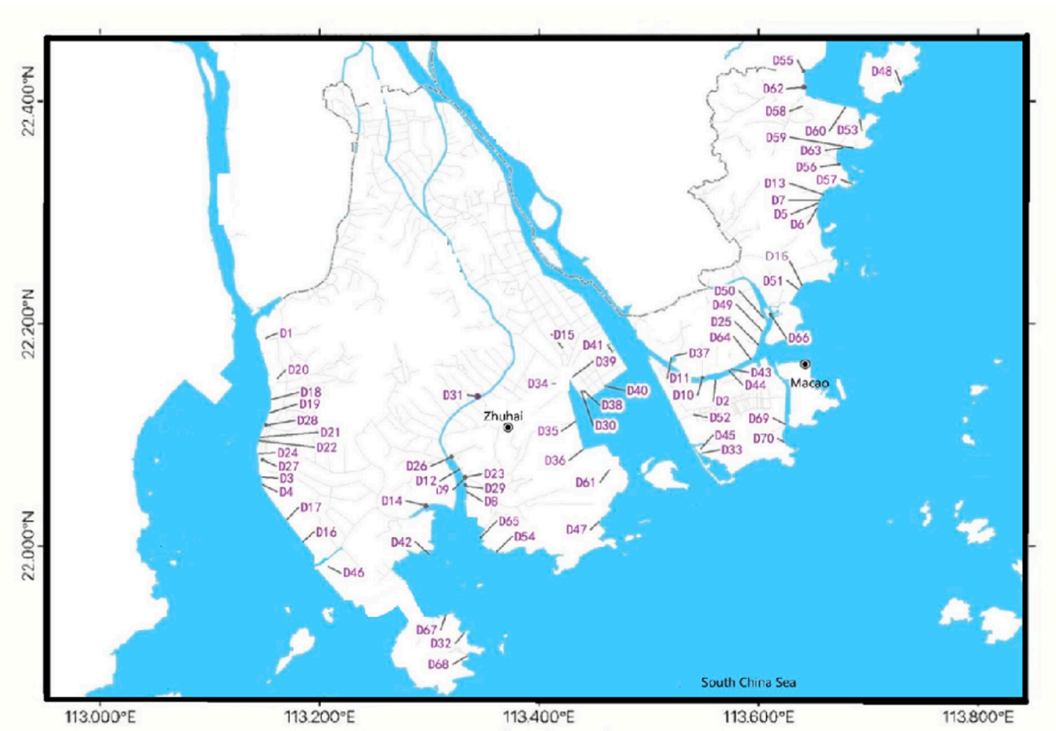

Fig. 1. Distribution of monitoring points.

2. Method

2.1. Point layout principles

Zhuhai City is located in the lower reaches of the Xijiang River and is situated on the coast. It has many rivers within its boundaries, making it a typical delta river network area. The main water systems passing through the city include the Modaomen, the Jitimeng, the Hutiaomen, and the Yamen. According to statistics, Zhuhai has a total of 487 river channels, excluding the four major water systems that flow into the sea. The study focuses on investigating the 70 river channels that flow into the sea in Zhuhai City. The sampling points are shown in Fig. 1.

2.2. Monitoring indicators, time and frequency

The water quality monitoring indicators include water temperature, chemical oxygen demand, flow rate, total organic carbon, total nitrogen(TN), ammonia nitrogen(NH_4-N), nitrate nitrogen(NO_3-N), and nitrite nitrogen(NO_2-N), etc. The river channels that flow into the sea along the coast (including drainage channels) are a total of 70, and on-site investigations were conducted in December 2021 and July 2022, respectively. If the sampling site is affected by tides, samples are collected at the lowest tidal stage.

2.3. Calculation of river channel discharge

River channels with sluice gates (drainage channels) - The discharge is measured when the sluice gate is opened (usually during the ebb tide period), and water samples are collected at the same time in the river channel where the tide has the least impact. Flow rate monitoring is carried out according to the characteristics of different river channels using acoustic Doppler current profiler (ADCP) profiling method, hydraulic structure measurement method, and current meter method, and water quality samples are collected simultaneously. Unregulated drainage channels and natural rivers - Sampling is conducted during periods when tidal influence on the river is minimal, typically at low tide. Flow monitoring is conducted using methods such as ADCP mobile measurement and velocity meter measurement, and water quality samples are collected simultaneously.

Underground streams - Sampling and monitoring are conducted at the point of discharge into the sea. If there is a sluice gate, measurement should be taken when the gate is opened, and if there is no sluice gate, measurement should be taken at low tide. Flow monitoring is conducted using methods such as ADCP mobile measurement, hydraulic structure flow measurement, and velocity meter measurement, and water quality samples are collected simultaneously based on the characteristics of different river channels.

2.4. Quality control

All samples were collected, monitored, and quality controlled in accordance with the requirements of the 《Surface Water

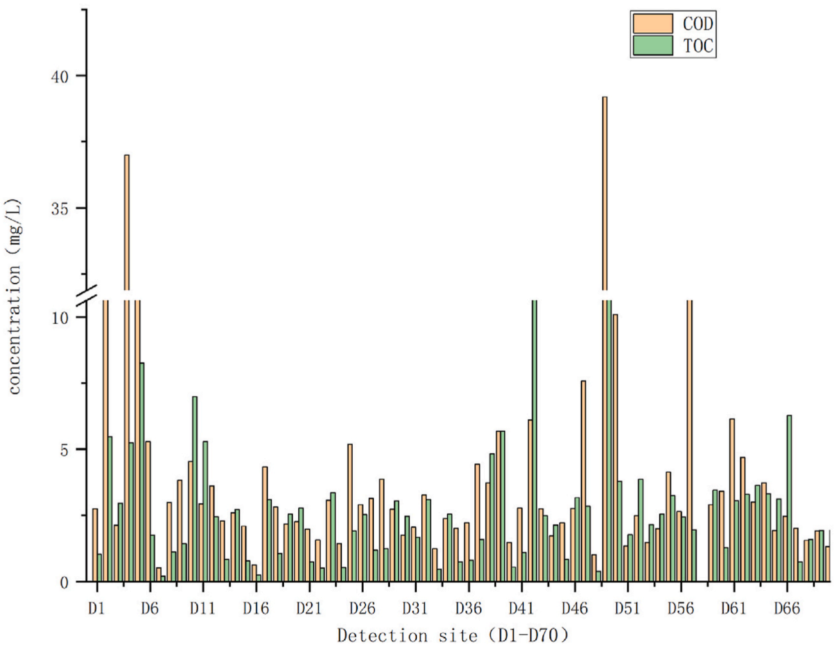

Fig. 2. Comparison of concentrations at each monitoring point in the dry season.

Environmental Quality Standards》(GB 3838-2002). In addition, all instruments were calibrated and certified to ensure accuracy.

3. Results and discussion

3.1. Monitoring results of carbon flux in hai river

3.1.1. Monitoring results of the Inhai river Swell in December

The monitoring results of total organic carbon ranged from 0.19 to 14.7 mg/L, with the highest value at D49 station 14.7 mg/L and the lowest value at D7 0.19 mg/L. Due to seawater inflow in winter, only 16 samples at the sampling points belong to surface water, and the salinity of the remaining samples is greater than 2 ‰. In order to facilitate the comparability analysis of data among the sampling points, the detection method of seawater chemical oxygen demand was used to determine the data statistics. The monitoring results ranged from 0.52 to 39.2 mg/L, with the highest value of 39.2 mg/L at D49 station and the lowest value of 0.52 mg/L at D7 station. The comparison between total organic carbon and chemical oxygen demand of seawater is shown in Fig. 2. In general, there is a strong correlation between total organic carbon and chemical oxygen demand, assuming that all organic matter can be completely oxidized. COD/TOC = 2O/C = 2.67, However, the oxidation capacity of potassium permanganate method is low, so the proportion will decrease.Through linear fitting, TOC(mg/L) = 0.3227* COD(mg/L). The highest values both appear in D49. The lowest values are all D7. Hydrological data were collected while monitoring all sections. The monitoring of the fluxes of total organic carbon and seawater chemical oxygen demand in sections was shown in Fig. 3. The monitoring results of total organic carbon fluxes ranged from 0 to 917.87 g/s, with the highest value at D31 917.87 g/s. The monitoring results of chemical oxygen demand flux ranged from 0 to 1121.35 g/s, and the highest value was D31 1121.35 g/s. The comparison of total organic carbon and chemical oxygen demand fluxes in seawater is shown in Fig. 3, with the highest values appearing in D31. Although the values of total organic carbon and seawater chemical oxygen demand at this site are not the highest, the flux calculation is the largest, mainly because the flow of the D31 gate waterway is the largest flow of all the monitored sites. In the dry season, the total discharge into the sea was 939.22 m^3/s, and the maximum discharge point was D31 547.00 m^3/s, accounting for 58.24 % of the total discharge. The total carbon flux was 1804.45 g/s, and the maximum D31 point was 917.87 g/s, accounting for 50.87 % of all organic carbon fluxes. The total COD flux was 2384.77 g/s, and the maximum D31 point of the flux was 1121.35 g/s, accounting for 47.02 % of the total COD flux.

3.1.2. Results of in July

The monitoring results of total organic carbon ranged from 1.04 to 10.95 mg/L, with the highest value at D50 site at 10.95 mg/L and the lowest value at D51 site at 1.04 mg/L. In this sample, the salinity of the samples was all less than 2 ‰, and the detection method of surface water COD was used to determine the monitoring results. The monitoring result was ranged from 5 to 36 mg/L, with the

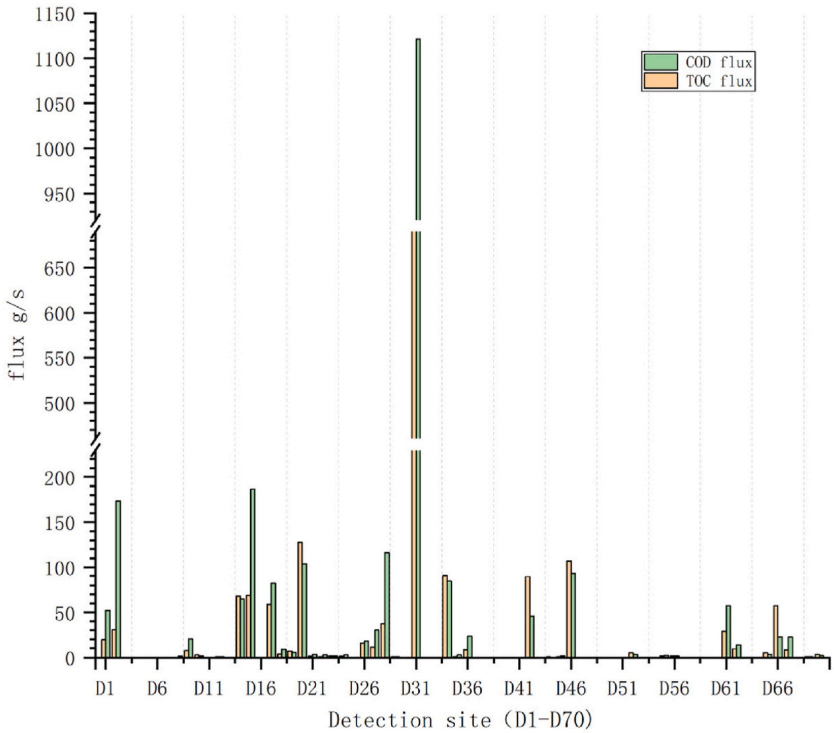

Fig. 3. Comparison of flux at each monitoring point in the dry season.

highest value being 36 mg/L at the D50 station and the lowest value being 5 mg/L at the D48 station. The comparison between total organic carbon and chemical oxygen demand is shown in Fig. 4, and the highest values are 10.95 mg/L at the D50 site. The lowest values are different, but the data are very similar. The total organic carbon and chemical oxygen demand values of D51 site are 1.05 mg/L and 9 mg/L. The total organic carbon and chemical oxygen demand values of D48 site are 1.56 mg/L and 5 mg/L. There is a strong correlation between the total organic carbon and the chemical oxygen demand flux. Through linear fitting, TOC(mg/L) = 0.2071* COD(mg/L). Hydrological data were collected while monitoring all sections. The monitoring of the fluxes of total organic carbon and seawater chemical oxygen demand in sections was shown in Fig. 5. The monitoring results of total organic carbon fluxes ranged from 0 to 2327.6 g/s, and the highest value was 2327.60 g/s at station D31. Higher values also include D15 site 162.85 g/s, D36 site 83.54 g/s, D37 site 96.27 g/s, D52 site 86.15 g/s, and D58 site 87.7 g/s points. Chemical oxygen demand flux monitoring results range from 0 to 8800.00 g/s, The highest value is 8800.g/s at the D31 site, and the higher value is 651.10 g/s at the D15 site, 459.00 g/s at the D36 site, 485.10 g/s at the D37 site, 442.00 g/s at the D52 site, and 428.40 g/s at the D58 site. The comparison between the fluxes of total organic carbon and chemical oxygen demand in seawater is shown in Fig. 5, and the highest values all appear in the D31 gate waterway. Although the values of total organic carbon and chemical oxygen demand were not the highest at this point, the flux was the largest, similar to the results in the dry season in December. The total flow into the sea in the wet season is 1556.40m^3/sm^3/s, and the maximum flow point is 1100.00 m^3/s at D31 station, accounting for 70.67 % of the total flow. The total carbon flux was 3331.04 g/s, and the largest point of flux was 2327.60 g/s at D31, accounting for 69.87 % of all organic carbon flux. The total COD flux was 13355.20 g/s, and the maximum flux point was 8800.00 g/s at D31 station, accounting for 65.89 % of all COD fluxes.

3.1.3. Data relationship of wet season and dry season

D31 station is located in Sanzao Town, Jinwan District, Zhuhai City, its upstream is the north-south drainage canal of Sanzao Town, Sanzao water purification plant drains into the downstream of the gate waterway, its basin covers the entire Sanzao Industrial zone. It is the point with the largest flow and flux in the two measurements. The flow rate in wet season was 1100 m^3/s, that in dry season was 547 m^3/s, and that in wet season was 2.01 times that in dry season. The organic carbon flux was 2327.6 g/s in wet season and 917.87 g/s in dry season, which was 2.54 times that in dry season. The chemical oxygen demand flux was 2310.00 g/s in wet season and 1121.35 g/s in dry season, which was 2.06 times of that in dry season. It is consistent with the data of 2.54 times of organic carbon flux in the same period, which further indicates the reliability of the monitoring data.

According to Wang Nan et al. [9]: According to the investigation results of the characteristics analysis of agricultural non-point source pollution sources in Guangdong Province from 1991 to 2021, it can be clearly found in the diagrams of pollutant emissions from livestock and poultry farming and aquaculture industry that the chemical oxygen intake is obviously similar to the total nitrogen emissions, and the total amount is comparable. Between 1991 and 2021, the annual growth rate of aquaculture pollutant emissions will average 24 %. Aquaculture is increasing year by year, and aquaculture is especially the construction of Marine pastures, so the amount of pollution from aquaculture and the proportion of pollutants emitted from agricultural sources will be increasing in the future. Through the monitoring of carbon flux, it can be further predicted that the intensity of total nitrogen emissions is not much

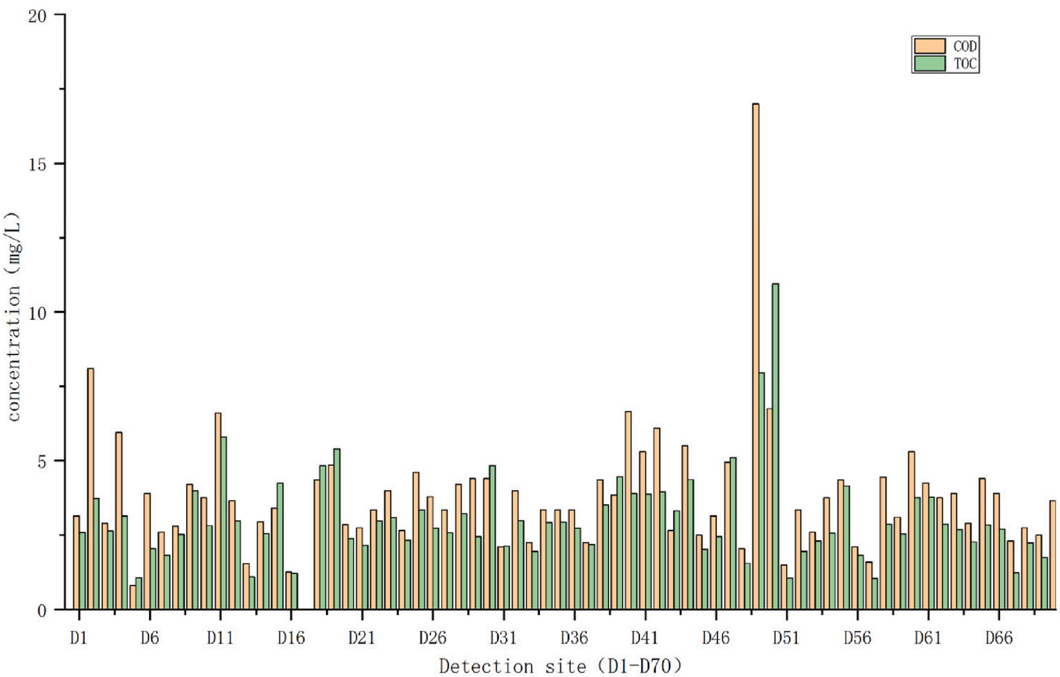

Fig. 4. Comparison of TOC and COD concentration at each monitoring point in the wet season.

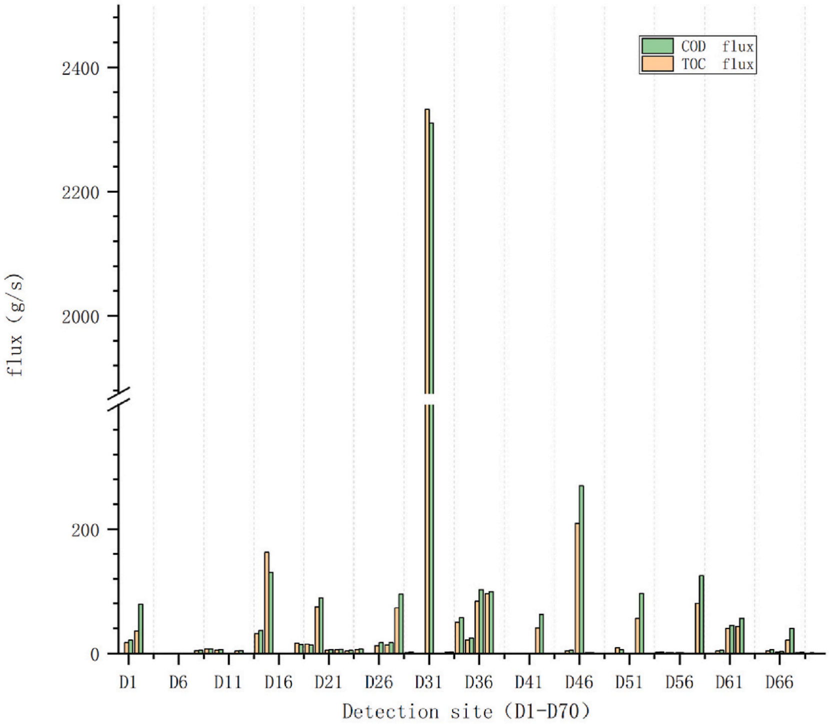

Fig. 5. Comparison of flux at each monitoring point in the wet season.

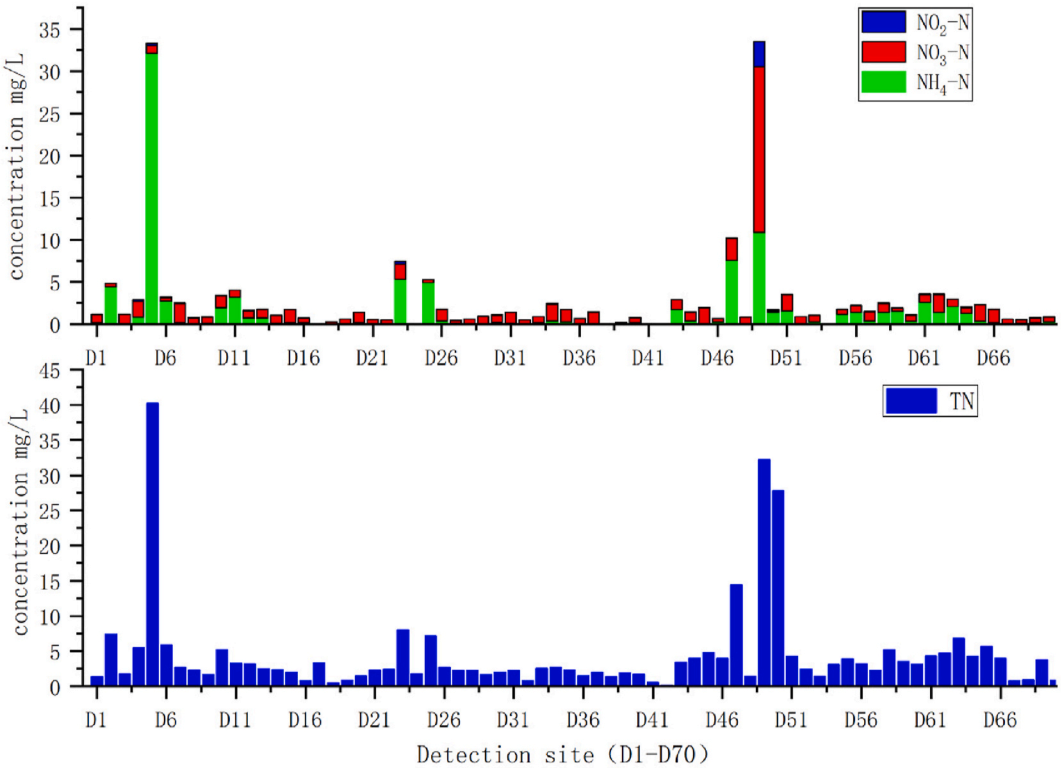

Fig. 6. Comparison of monitoring results of total nitrogen and inorganic nitrogen during dry season.

different from that of chemical oxygen demand, which provides data reference for the prevention and control of total nitrogen pollution in the coastal waters of the Pearl River Estuary.

3.2. Monitoring results of nitrogen flux in Haihe River

3.2.1. Monitoring results of concentration flux during the low water period in Lihai river

The monitoring results of total nitrogen, ammonia nitrogen, nitrate nitrogen and nitrite nitrogen during dry season are shown in Fig. 6. The monitoring results of total nitrogen range from 0.19 to 40.20 mg/L, with the highest value located at D5 station 40.20 mg/L. Total nitrogen and inorganic nitrogen (ammonia nitrogen, nitrate nitrogen, nitrite nitrogen) showed an obvious correlation trend, and the inorganic nitrogen proportion of ammonia nitrogen in D5 site was the highest, and the concentration of ammonia nitrogen was as high as 32.10 mg/L. The nitrate nitrogen in site D49 was 19.60 mg/L. D50 site is the most special, with total nitrogen as high as 27.80 mg/L, inorganic nitrogen only 1.76 mg/L, organic nitrogen concentration 26.04 mg/L. Chemical oxygen demand (COD), five-day biochemical oxygen demand (BOD5), total phosphorus (TP) and other indicators were simultaneously detected on water samples from D50 site. The detected concentration of COD is only 83.00 mg/L, but BOD5 is as high as 64.60 mg/L and total phosphorus is 1.90 mg/L, indicating that the water body in this area has received infiltration pollution from domestic water bodies.

The total flow into the sea during dry season is 939.22 m^3/s, and the maximum flow point is 547.00 m^3/s at D31 station, accounting for 58.24 % of the total flow. The total nitrogen flux was 2204.68 g/s, and the maximum nitrogen flux was 1241.69 g/s at D31 station, accounting for 56.32 % of all nitrogen fluxes. Although the value of total nitrogen at this site was not the highest, the flux was the largest, mainly due to the fact that the D31 site had the highest flow of all the monitored sites. According to Fig. 7, we can also find that there is a great correlation between total nitrogen and inorganic nitrogen flux, which is mainly due to the positive correlation between total nitrogen and inorganic nitrogen. At the same time, the cross section with a large flux has a larger flow rate.

3.2.2. Results of concentration flux during the high water period

The monitoring results in wet season are shown in Fig. 8. The monitoring results of total nitrogen ranged from 0.28 to 17.80 mg/L. The highest value is located at D49, and the lowest value is located at D38. The comparison of flow, concentration and flux in wet season is shown in Fig. 9. The total flow into the sea in wet season is 1556.40 m^3/s, and the maximum flow point is 1100.00 m^3/s at D31 station, accounting for 70.67 % of the total flow. The total nitrogen flux was 2403.47 g/s, and the maximum point of the flux was 1727.00 g/s at D31 station, accounting for 71.85 % of all nitrogen fluxes.

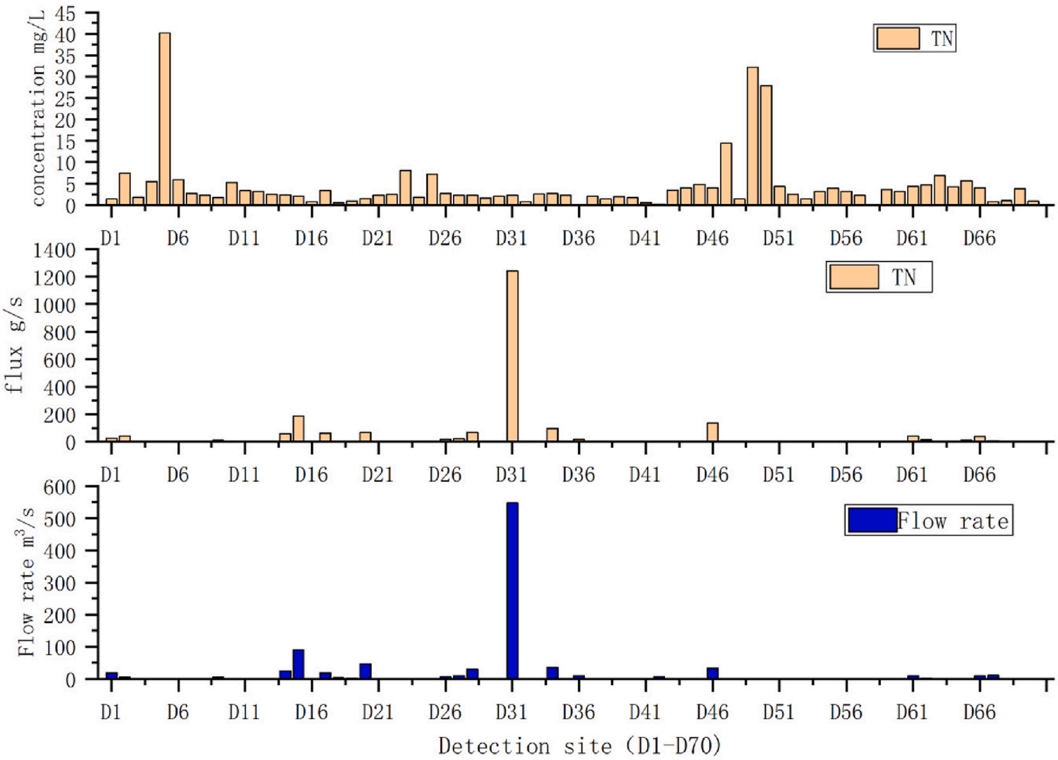

Fig. 7. Comparison of total nitrogen flux, flow and concentration during dry season.

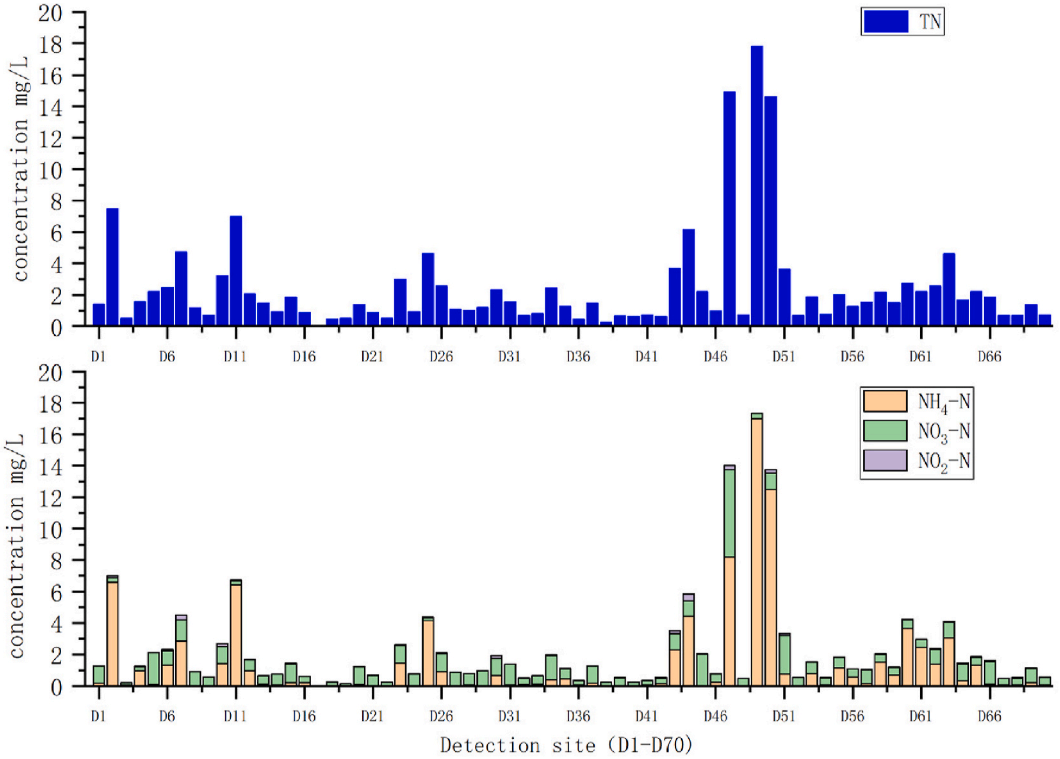

Fig. 8. Comparison of monitoring results of total nitrogen and inorganic nitrogen concentration in wet season.

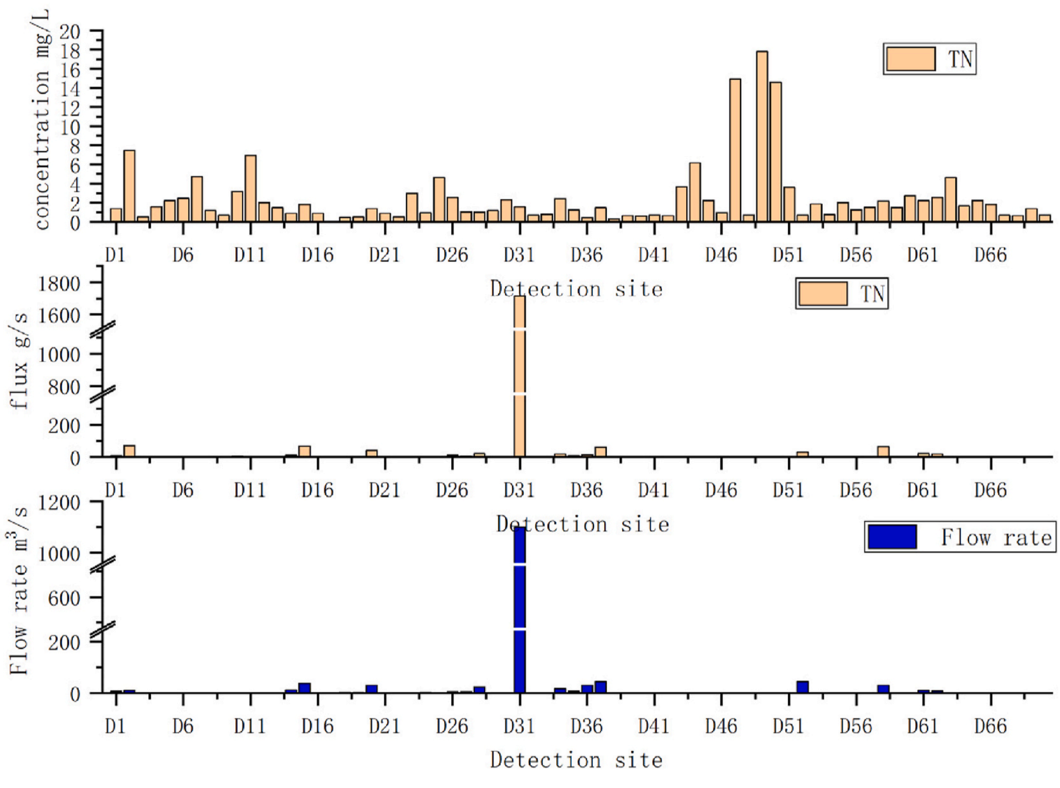

Fig. 9. Monitoring results of total nitrogen and inorganic nitrogen in wet season.

3.2.3. Comparison of detection results of Inhai river swell

The maximum concentration of total nitrogen was higher in dry season (40.20 mg/L) than in wet season (17.80 mg/L). The highest concentration of the three times was measured at D49 station, and the points with high concentration had relatively small flow and poor water circulation. Through the superposition comparison of the flow of the three periods, it can be clearly found (Fig. 10) that the total flow of the dry period (939.22 m^3/s) < the wet period (1556.40 m^3/s), and the maximum flow point of the three times are all at the D31 station, which is the main reason why this point is the maximum flux point. The largest flow points are all at D31, mainly because upstream of this point is the Sanzao Water Purification Plant, which collects domestic and industrial sewage from the entire area and provides a stable water source for the waterway. The total nitrogen flux in the dry period (2204.68 g/s) < the wet period (2403.47 g/s), and the wet period was lower than the normal period, which may be due to the lush summer plants, and the nitrogen in the water can be directly absorbed and utilized by plants and algae, and the lush growth of plants leads to the absorption and transformation of a large amount of ammonia nitrogen. According to the Bulletin on the State of China's Marine Ecological Environment released in recent years, the main overstandard factors in the South China Sea area are total nitrogen, chemical oxygen demand, potassium permanganate index, total phosphorus and other indicators, which echo the results of this batch of surveys.

4. Conclusions

According to the results of traceability, it is necessary to coordinate upstream and downstream efforts and implement joint pollution prevention and control with upstream cities. In Zhuhai City, we need to strengthen pollution prevention and control of river inflow into the sea, and conduct "tracking monitoring - pollution traceback - remediation countermeasures preparation" for high-pollution inflows detected in the early stages. Additionally, accurate investigation and treatment of sewage discharge outlets for key intakes into Haihe River should be carried out, promoting comprehensive remediation of polluted river reaches and river ecological restoration. Improvements in front-end collection can effectively reduce wastewater discharge into rivers, thereby reducing pollution and carbon emissions. Simultaneously, the upgrading of sewage treatment facilities should be accelerated to improve efficiency. Pollution type-specific measures should be implemented to improve water quality. Strengthening total nitrogen reduction at sewage treatment plants through constructed wetlands will compensate for urban domestic sewage collection deficiencies. By increasing the inlet BOD concentration at sewage treatment plants, total nitrogen concentration in inlet water can be increased. Constructed wetlands downstream of sewage treatment plants can further reduce total nitrogen by treating tailwater according to local conditions.

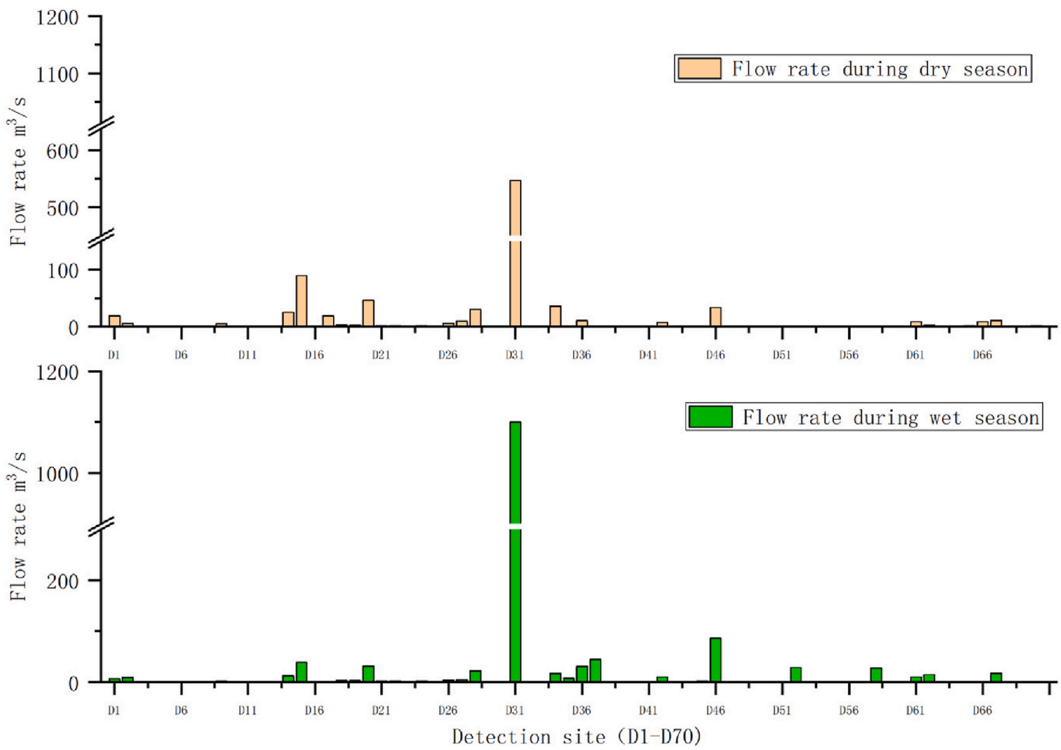

Fig. 10. Comparison of flow during dry season and wet season.

CRediT authorship contribution statement

Dawei Li: Conceptualization. **Hongji Liang:** Formal analysis, Data curation. **Zimiao Zhao:** Resources, Project administration. **Huifeng Huang:** Resources. **Cuiming Li:** Project administration. **Chengzhi Wang:** Writing – review & editing, Supervision.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Declaration of competing interest

I,Dawei Li, and all authors,declare that there are no conflicts of interest in relation to the manuscript titled "Monitoring and Discussion on River Carbon and Nitrogen Fluxes in the Pearl River Estuary Region" submitted to Heliyon. we confirm that the results and interpretations reported in the manuscript are original and have not been plagiarized.

I certify that I have read and understand the Heliyon conflict of interest policy, and I understand that failure to disclose a conflict of interest may result in the manucript being rejected or retracted.

I confirm that I have no known conflicts of interest that would influence the results or interpretation of the data presented in this manuscript, and I understand that failure to disclose a conflict of interest is unethical and may result in sanctions being imposed on me.

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