Variation of total phosphorus concentration and loads in the upper Yangtze River and contribution of non-point sources

Qian Li, Zhonghua Yang, Yao Yue, Hua Zhong and Da Li

ABSTRACT

Excessive phosphorus has become the primary reason for the deterioration of the water quality of the upper Yangtze River Basin. Here, we comprehensively study variations in total phosphorus (TP) concentration and TP loads in the upper reach of the Yangtze River during 2004–2017 (after the impoundment of the Three Gorges Dam). Non-point source TP loads flowing into the mainstream are also analyzed based on the base flow segmentation method. TP concentration in the mainstream showed a fluctuating trend of decreasing–increasing–decreasing from 2004 to 2017. TP loads from tributaries had a greater impact on TP concentration in the mainstream than the retention effect. Non-point source was an important source of TP loads. Average TP loads from non-point source pollution were 24.9×10^6 kg per year, contributing about 50.8% of the TP loads from 2004 to 2017. Non-point source TP loads were mainly from Jinsha River and Jialing River, accounting for 59.1% of total non-point TP loads, and they mainly occurred in the wet season. The long-term variation trend of TP loads from tributaries was affected by economic development, intensity of pollution control and significant discharge change. In terms of pollution control, we suggest comprehensive treatment of point and non-point source pollution.

Key words | loads, mainstream, non-point source, point source, total phosphorus, tributary

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HIGHLIGHTS

- TP concentration of mainstream showed a trend of decreasing–increasing–decreasing.
- TP loads from tributaries had a greater impact on TP concentration in the mainstream than the retention effect.
- Average TP loads from non-point source pollution contributed about 50.8% of total TP loads.
- Long-term variation trend of TP loads was affected by economic development, intensity of pollution control and significant discharge change.

INTRODUCTION

In recent decades, phosphorus loads have intensified markedly (Peñuelas *et al.* 2012, 2013; Tong *et al.* 2017b). Phosphorus is the crucial controlling factor that causes algal blooms and it is one of the key elements of eutrophication (Liu *et al.* 2016b). Worldwide, excessive phosphorus has led to serious environmental problems and has caused the degradation of water quality (Carpenter 2008; Conley *et al.* 2009; Stone 2011; Liu *et al.* 2016a).

In the Yangtze River Basin (YRB), the socioeconomic system has developed greatly in recent years (Liu *et al.* 2018).

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Large anthropogenic activities have resulted in poor water quality (Han *et al.* 2016). Water quality deterioration has been the main concern in the YRB (Huang *et al.* 2012). Phosphorus has shown remarkable rising trends in the YRB from 1970 to 2000 (Powers *et al.* 2016; Ding & Liu 2019). In the YRB, the total phosphorus (TP) pollution used to be heaviest in the upper YRB, and phosphorus has become the main pollution nutrient factor in the basin since 2016 (Qin *et al.* 2018). The Chinese government realized the seriousness of phosphorus pollution in the upper YRB and implemented corresponding treatment measures to improve water quality by controlling TP sources in recent years. Understanding spatiotemporal variations of TP concentration are important for water quality management and evaluation (Han *et al.* 2016). Most previous studies have mainly focused TP concentration and loads on shorter time series and partial areas in the upper YRB such as Jinsha River (Lu *et al.* 2011) and the Three Gorges Reservoir (TGR) (Ran *et al.* 2016; Xia *et al.* 2018). Few studies have studied long-term variations in TP concentration and loads on the entire upper YRB, especially in recent years. In the upper Yangtze River, more than 90% of the TP loads in the mainstream come from the five tributaries (Tong *et al.* 2017a). In June 2003, the impoundment of the Three Gorges Dam (TGD) was completed. It is necessary to study TP concentration and loads in the mainstream and tributaries of the upper Yangtze River after the impoundment of TGD.

River phosphorus is mainly from point source and non-point source (NPS) pollution, such as soil erosion, agricultural fertilizer, and waste water (Sun *et al.* 2013). Estimation of point and non-point source TP loads is of great significance for phosphorus pollution control. Traditional models, including SWAT, Export Coefficient Model and AnnAGNPS can accurately estimate NPS-TP loads (Li *et al.* 2015; Zhang *et al.* 2020). However, it is difficult to build these models because most of these models need vast, high-quality data. NPS pollution load estimation based on the base flow segmentation method is simple and has fewer data requirements. Thus it has been well applied in some watersheds such as Poyang Lake and Danjiangkou Reservoir (Tu *et al.* 2012; Xin *et al.* 2017). In addition, previous studies mainly estimated NPS-TP loads of the upper YRB (Shen *et al.* 2013; Ding & Liu 2019; Ding *et al.* 2019). Few studies have quantified the contributions of NPS-TP loads to total TP loads.

The objective of this study was to (i) investigate long-time variation characteristics of TP concentration in the upper YRB after the impoundment of TGD and identify heavily polluted areas, (ii) analyze variations in TP loads of the upper Yangtze River and (iii) calculate NPS-TP loads based on the base flow segmentation method and quantify its contributions to total TP loads. The results will provide helpful information to control the TP concentration and loads in the upper YRB.

MATERIALS AND METHODS

Study area

The upper reaches of the Yangtze River mainstream extend over 1,040 km from Yibin to Yichang with five main tributaries. The five main tributaries are the Jinsha River, Min River, Tuo River, Jialing River, and Wu River. The Jinsha River lies on the upstream of the upper Yangtze River. The Min River, Tuo River, and Jialing River are in the north of the mainstream and the Wu River is in the south. There are seven TP sampling stations in the mainstream, which are Yibin, Cuntan, Fuling, Tuokou, Shilipu, Guandukou, and Taipingxi stations. The stations on the tributaries are Yibin (Jialing River), Gaochang, Wangjianglou (Min River), Sanhuangmiao, Fushun (Tuo River), Nanchong, Linjiangmen, Xiaoheba (Jialing River), Guiyang, Wulong, and Zunyi (Wu River) (Figure 1). Yibin station is the boundary between the mainstream and the Jinsha River, and it serves as the TP monitoring station for both Jinsha River and the mainstream.

Data sources

The TP concentration was monitored on a monthly basis from 2004 to 2017, while discharge data of the Jinsha River, Min River, Jialingjiang, Wu River, Tuo River and Yichang station were on a daily basis. Data were obtained from the Yangtze River Water Resources Commission, which is the official YRB management agency. The locations of the 17 sampling stations are shown in Figure 1.

Sample collection and measurement

At each site, three replicates were collected at three different depths (surface, intermediate and near-bottom) at each

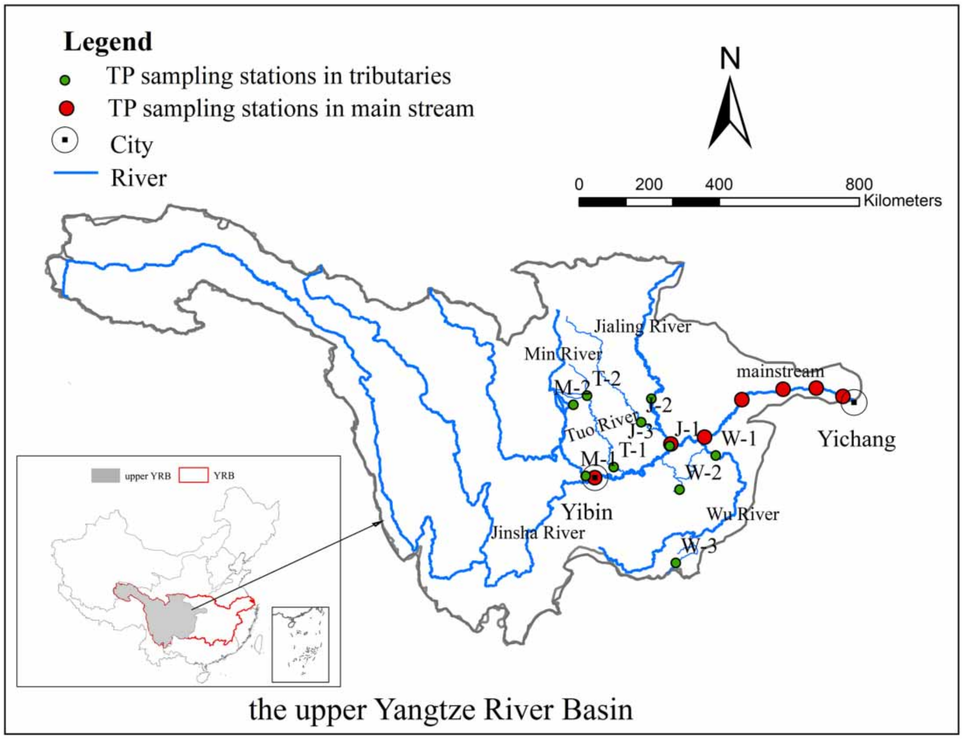

Figure 1 | Map of the upper YRB and TP monitoring stations. The red dots represent the TP sampling stations on the mainstream. They are Yibin, Cuntan, Fuling, Tuokou, Fengjie, Badong, and Taipingxi stations from left to right. The green dots represent the TP sampling stations on the tributaries. The TP sampling station on the Jinsha River is the Yibin station. M-1 and M-2 represent the Gaochang and Wangjianglou stations on the Min River, respectively. T-1 and T-2 represent the Fushun and Sanhuangmiao stations on the Tuo River, respectively. J-1, J-2, and J-3 represent the Linjiangmen, Xiaohe, and Nanchong stations on the Jialing River, respectively. W-1, W-2, and W-3 represent the Wulong, Zunyi, and Guiyang stations on the Wu River, respectively. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/ws.2021.015.

station with 500 mL high density polyethylene containers that had been acid-washed in advance. The samples were subsequently well mixed *in situ*, and the containers were rinsed with sample water before sampling. All water samples were kept at 4°C and returned to the laboratory for analysis. The concentration of TP was measured with the ammonium molybdate spectrophotometric method following the standard methods in GB11893-89.

Calculation of average TP concentration and classification of water quality

The yearly average TP concentration is calculated using the average value of 12 months. The average TP concentration in the mainstream is calculated using the average value of all TP sampling stations on the mainstream. TP concentration of tributaries is the average value of all TP sampling stations on the tributaries.

Water quality can be divided into five grades in accordance with the surface water quality standard of China (GB3838-2002) (Lu *et al.* 2011). Grades I, II, and III represent water that is potable after conventional water treatment, whereas Grades IV and V represent water that is in the most polluted state. The thresholds of TP for different water quality grades in GB3838-2002 of China are shown in Table 1. The management requirements for water quality in the upper YRB are in Grade III, with TP

Table 1 | Evaluation standard of TP from environmental quality standards for surface water (GB3838-2002) in China

Water quality classification	TP (mg/L)
Grade I	≤0.02 (lake and reservoir 0.01)
Grade II	≤0.1 (lake and reservoir 0.025)
Grade III	≤0.2 (lake and reservoir 0.05)
Grade IV	≤0.3 (lake and reservoir 0.1)
Grade V	≤0.4 (lake and reservoir 0.2)

concentration threshold values of 0.2 mg/L in the mainstream and tributaries and 0.05 mg/L in the TGR (CSEPB 2002).

Mann–Kendall test

The analysis and judgment of the change trend of water quality are important parts of water quality evaluation, and the objective is to determine the laws of the change trend with time. The Mann–Kendall (M-K) test is a non-parametric method. It has been widely used to test the trends of hydro-climatic and water quality time series (Li *et al.* 2020).

The null hypothesis, H_0, is that there is no trend in the time series. The alternative hypothesis, H_1, is that there is an upward trend or downward trend. The test statistic is the Z value. $Z > 0$ represents upward trends, while $Z < 0$ represents downward trends over time. This study applied a confidence level of 5% ($\alpha = 0.05$), which means any $|Z| > 1.96$ representing a trend is significant and the null hypothesis is rejected (Helsel & Frans 2006).

Z can be calculated by the following formulas:

$$S = \sum_{i=1}^{n=1} \sum_{j=i+1}^{n} \operatorname{sgn}(x_j - x_i), \tag{1}$$

$$\operatorname{sgn}(x_i - x_j) = \begin{cases} +1 & \text{if } (x_i - x_j) > 0 \\ 0 & \text{if } (x_i - x_j) = 0 \\ -1 & \text{if } (x_i - x_j) < 0 \end{cases}, \tag{2}$$

$$\operatorname{var}(s) = \frac{1}{18}[n(n-1)(2n+5)], \tag{3}$$

$$Z = \begin{cases} \dfrac{s-1}{\sqrt{\operatorname{Var}(s)}} & \text{if} \quad s > 0 \\ 0 & \text{if} \quad s = 0 \\ \dfrac{s-1}{\sqrt{\operatorname{Var}(s)}} & \text{if} \quad s > 0 \end{cases}, \tag{4}$$

where Var(s) is variance; x_i and x_j are the sequential data values at time i and j; Z is the test statistic.

Base flow segmentation

Total runoff can be divided into surface runoff and base flow (Smakhtin 2001). Base flow segmentation is a method of separating base flow from total runoff. Many methods have been used to segment base flow from runoff (Eckhardt 2005; He & Lu 2016; Xie *et al.* 2020). One of the most widely used methods has been the digital filtering method. It was proposed by Lyne and Hollick in 1979, and its core is the filtering equation (Lyne & Hollick 1979):

$$q_t = \beta q_{t-1} + \frac{1+\beta}{\alpha}(Q_t - Q_{t-1}), \tag{5}$$

where q_t is the filtered discharge on the t-th day, Q_t is the total discharge on the t-th day, α and β are the filter parameters; and the filtered base flow is defined as $Q_t - Q_{t-1}$. Nathan & McMahon (1990) recommended that α and β be 2.0 and 0.925.

Flux estimates

After the base flow is segmented, we can estimate NPS-TP load. TP load transported in the base flow represents point source TP load. And TP load transported in surface runoff represents NPS-TP load (Xin *et al.* 2017). The annual total TP loads are:

$$W_t = \int_0^t [C_p(t)Q_p(t) + C_{np}(t)Q_{np}(t)]dt, \tag{6}$$

where t is time; $C_p(t)$ is the TP concentration during the dry season; $Q_p(t)$ is the base flow; $C_{np}(t)$ is the TP concentration of NPS at time t; Q_{np} is the surface runoff; W_t is total TP loads. Because of the lack of continuous water quality data, Equation (2) needs to be discretized:

$$W_t = \sum_{i=1}^{n} C_{pi}Q_{pi}\Delta t + \sum_{i=1}^{n} C_{npi}Q_{npi}\Delta t, \tag{7}$$

where W_t can be directly obtained from the water quantity data of the monitoring stations:

$$W_t = \sum_{i=1}^{n} C_i Q_i \Delta t. \tag{8}$$

Since the monitoring frequency of TP concentration is one month, C_i (mg/L) is TP concentration in the i-th month. When the TP loads flowing into the mainstream from tributaries are calculated, TP concentration is selected from the station nearest to the mainstream. The stations on tributaries are Yibin (Jinsha River), Gaochang (Min River), Fushun (Tuo River), Linjiangmen (Jialing River), and Wulong (Wu River). Q_i (m^3/L) is the monthly average discharge in the i-th month; Δt is one month in this paper.

Point source TP load can be represented:

$$W_p = Q_p C_p \Delta t_p. \quad (9)$$

NPS-TP load can be represented as:

$$\sum_{i=1}^{n} C_{npi} Q_{npi} \Delta t = \sum_{i=1}^{n} C_i Q_i \Delta t - Q_p C_p \Delta t. \quad (10)$$

The above formula is the estimation formula of the NPS-TP load. NPS-TP load is estimated by subtracting point source TP load from total TP load. Point source TP load is estimated by the measured TP concentration in the dry season and the base flow.

RESULTS AND DISCUSSIONS

Variation in total phosphorus concentration in the mainstream

Yearly average TP concentration ranged from 0.085 mg/L to 0.174 mg/L with an average of 0.127 mg/L from 2004 to 2017 in the upper reaches of the Yangtze River mainstream. It showed a slight downward trend from 2004 to 2007, and then increased to 2012, and then sharply decreased from 2012 to 2017 (Figure 2(a)). And trends were significant in the periods of 2007–2012 and 2012–2017 according to the results of the Mann–Kendall test (Table 2). The highest yearly average TP concentration (0.174 mg/L) was observed

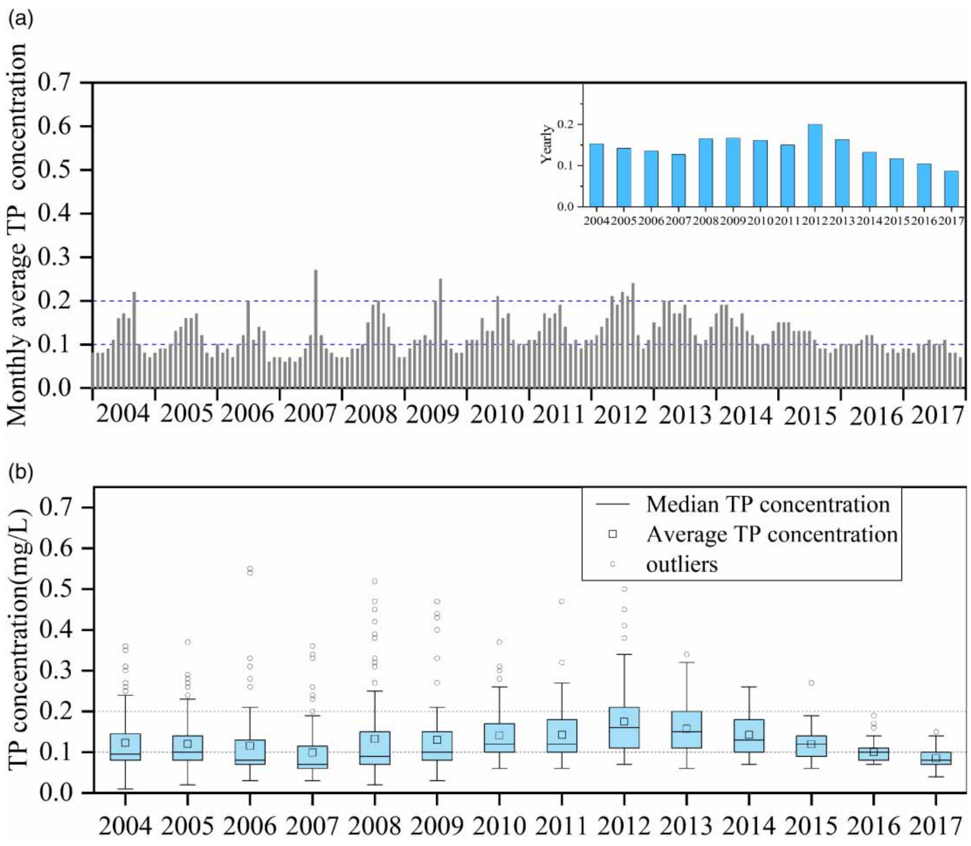

Figure 2 | (a) Variations in monthly and yearly average TP concentrations of seven sites on the mainstream from 2004 to 2017. (b) Monthly TP concentration at all the sampling sites on the mainstream from 2004 to 2017. The lengths of the boxes indicate the inter-quartile range of TP concentrations.

Table 2 | Mann–Kendall test results in yearly average TP concentration in the periods of 2004–2007, 2007–2012, 2012–2017, respectively

Z	Mainstream	Jinsha River	Min River	Tuo River	Jialing River	Wu River
2004–2007	− 1.70	− 0.34	− 1.70	− 0.34	− 0.34	− 0.34
2007–2012	2.25*	2.25*	0.37	1.88	1.13	1.50
2012–2017	− 2.63*	− 1.88	− 0.75	1.50	− 0.75	− 1.13

*Indicates Z exceeds the critical value of ±1.96 ($\alpha = 0.05$), representing the trend as significant. $Z > 0$ and $Z < 0$ represented the time series for TP concentration having an upward trend and a downward trend.

in 2012. And the median TP concentration showed similar trends in Figure 2(b). The monthly TP concentration at all the sampling sites in the mainstream were used to generate Figure 2(b). In 2004, less than 25% of monthly TP concentrations were above 0.2 mg/L (the maximum value of Grade III by China's water quality standard), and in 2007 only outliers did not meet water quality requirements (Grade III). In 2012, more than 25% of sample data had monthly TP concentrations higher than 0.2 mg/L, while none of the monthly concentrations was larger than 0.2 mg/L in 2017. These observations indicated that the water quality of the mainstream improved first and then deteriorated, and finally got a great improvement. The outliers occurred mainly in July and August, and mainly in Cuntan and Fuling stations, which may be related to a large amount of TP loads from tributaries flowing into the mainstream in summer. After 2012, the outliers gradually decreased, which indicated that TP concentration not only decreased but also tended to be stable after 2012 (Figure 2(b)).

Larger TP concentration was mainly observed in the wet season (June, July, August, and September) from 2013 to 2017. Lower TP concentration mainly occurred in the dry season (January, February, March, and December) from 2004 to 2012, but it was in the normal season (April, May, October, and November) from 2013 to 2017 (Figure 2(a)). Seasonal fluctuations in TP concentration can be attributed to the wide seasonal variations in precipitation and sediment discharge year-round (Lu *et al.* 2011). In the wet season, frequent storm events resulted in a lot of suspended sediment, which carried a large amount of phosphorus, flowing into the mainstream. Higher temperature in summer promoted the release of phosphorus adsorbed in the sediment (Tang *et al.* 2020). Therefore, TP concentration was largest in the wet season. From 2004 to 2012, sediment flowing into the mainstream in the dry season was smallest because of minimum precipitation, so TP concentration was lowest. In the period of 2013–2017, because of the operation of the Jinsha River cascade reservoirs in 2013 (Liu *et al.* 2019) and the control of soil erosion by the Chinese government in recent years, sediment flowing into the mainstream was reduced. Therefore, the difference of sediment between the normal and dry season was reduced. Compared with the dry season, the dilution effect caused by the increase of discharge in the normal season reduced TP concentration, so TP concentration in the normal season was minimum.

Figure 3 shows the longitudinal variations in yearly TP concentration along the mainstream. The yearly TP concentration from Yibin to Fuling increased at most times during the period of 2003–2017, which was mainly due to the import of the main tributaries. In contrast, TP concentration showed a fluctuating decline from Fuling to Taipingxi station. Several factors could contribute to this phenomenon. On the one hand, inflow TP loads from tributaries decreased. On the other hand, phosphorus accumulated at the bottom of the TGR with the depositional effect of sediments and was released under the proper conditions.

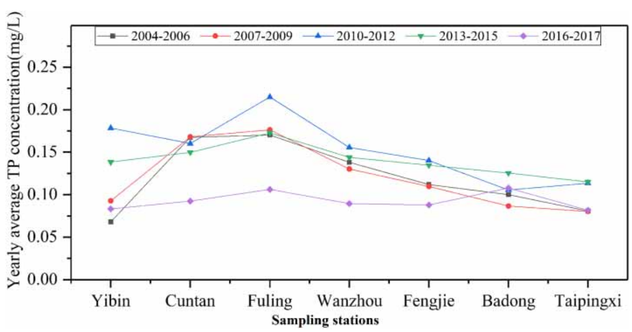

Figure 3 | Yearly and longitudinal variations in TP concentration along the mainstream.

Variation in total phosphorus concentration in the tributaries

The results of the Mann–Kendall test showed that variation trends of TP concentrations in most tributaries were decreasing–rising–decreasing, while TP concentration in the Tuo River showed upward trends in both the periods of 2007–2012 and 2012–2017. The majority of trends were insignificant according to the results of the Mann–Kendall test (Table 2). Yearly average TP concentration in tributaries are shown in Figure 4. and the monthly TP concentrations at all the sampling sites on tributaries are shown in Figure S1. The TP concentrations in the tributaries showed great spatial heterogeneity (Figure 4). The Wu River, Min River and Tuo River have higher TP concentrations. The yearly average TP concentration in the Wu River was the highest and it ranged from 0.654 mg/L to 0.245 mg/L. Phosphorus pollution in the Wu River was most serious. Yearly average TP concentrations in Min River and Tuo River were mainly in Grade IV or Grade V, which did not meet the water quality requirement of Grade III. Jialing River had the lowest and most stable yearly average TP concentration, which maintained at Grade II from 2004 to 2017. Besides 2012, the yearly TP concentration of Jinsha River was mainly in Grade III and Grade II.

Great spatial heterogeneity in TP concentration was mainly due to the difference of human activities. The mine exploitation and chemical pollution sources of phosphorus in the Wu River Basin and Min-Tuo Basin were the main reasons for the high concentration (Qin *et al.* 2018). Furthermore, 30% of basin areas were crop land around the Wu River, so the non-point source pollution was very severe (Han *et al.* 2016). Therefore, the Wu River was the most polluted tributary, followed by the Min and Tuo Rivers. It is worth noting that the TP concentrations in most tributaries showed downward trends in recent years (from 2012 to 2017), which was attributed to the effective control of phosphorus pollution by the Chinese government. TP concentration in the Tuo River presented an upward trend after 2012 due to its small discharge and weak self-purification capacity.

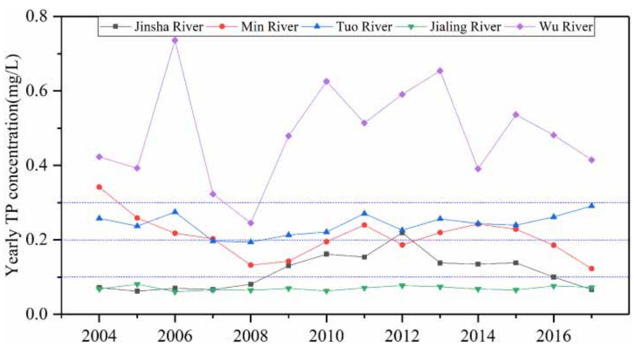

Figure 4 | Yearly average TP concentrations in tributaries.

Estimation of pollution loads

River base flow separation

Yichang station is the key hydrological station which measures water discharge in the mainstream of the upper Yangtze River (Zhou *et al.* 2013). Average total discharge of the five tributaries accounted for 81% of the average discharge in Yichang station (Table 3). It was representative to estimate TP loads from the five tributaries. Average discharge of the dry season (January, February, March, and December) accounted for 13.8% of the annual runoff (Table 3). The digital filtering method was used to calculate base flow (Figure S2). The average base flows of Jinsha River, Min River, Tuo River, Jialing River, and Wu River accounted for 62%, 56%, 42%, 30%, and 46% of their runoff (Table 3).

Long-term variation of total phosphorus loads and the contribution of non-point sources

Figure 5(a) shows the yearly total TP loads into the mainstream from the five main tributaries and discharge-weighted yearly average TP concentration of the

Table 3 | Average discharge and base flow of every tributary from 2004 to 2017

River	Station	Average discharge m^3/s	Total runoff 10^8 m^3	Average base flow m^3/s	Base flow runoff 10^8 m^3
Jinsha River	Pingshan	473	1,348	2,656	838
Min River	Gaochang	2,468	778	1,374	433
Tuo River	Fushun	349	110	146	46
Jialing River	Beibei	1,885	594	574	181
Wu River	Wulong	1,276	402	584	184
Mainstream	Yichang	12,557	3,959		

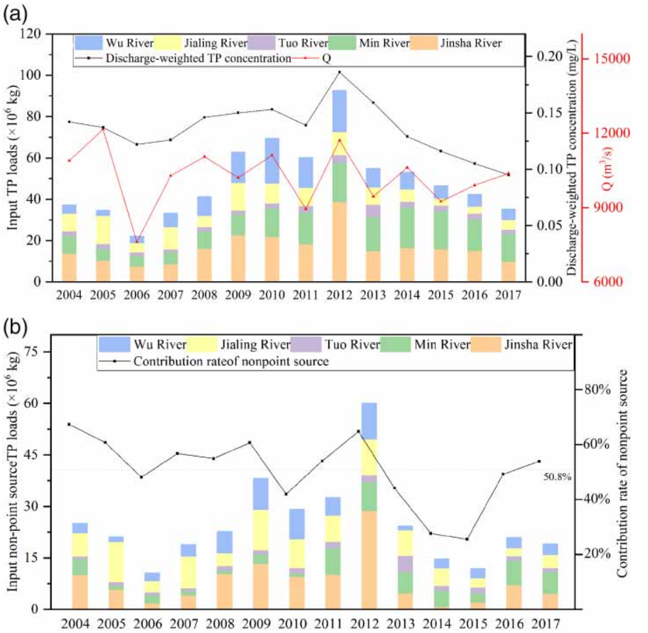

Figure 5 | (a) Yearly TP loads flowing into the mainstream from the five main tributaries, discharge-weighted yearly average TP concentration of mainstream and yearly discharge (Q) flowing into the mainstream from the five main tributaries from 2004 to 2017. (b) Yearly NPS-TP loads flowing into the mainstream from the five main tributaries from 2004 to 2017. The column represents input NPS-TP loads from the five main tributaries. The black line stands for contribution rate of NPS-TP loads to total TP loads in every year. The gray dotted line represents the contribution rate of NPS-TP loads to TP loads in the 14 years.

mainstream from 2004 to 2017. Input total TP loads showed a declining trend from 2004 to 2007, and then increasing to 2012, and then sharply decreasing from 2012 to 2017. It ranged from 22.1×10^6 kg in 2006 to 92.6×10^6 kg in 2012 with an average of 49×10^6 kg from 2004 to 2017. In order to avoid variations in flow conditions from year to year influencing the TP concentration, the discharge-weighted yearly average TP concentration of the mainstream was calculated. Similar to the trend of yearly average TP concentration, discharge-weighted yearly average TP concentration in the mainstream showed a fluctuating trend of decreasing–increasing–decreasing from 2004 to 2017. The discharge-weighted yearly average TP concentration in the mainstream changed simultaneously with yearly input TP load from the five tributaries, indicating that the total TP loads from the tributaries affected the TP concentration of the mainstream.

NPS-TP loads were estimated by the base flow segmentation method (Figure 5(b)). Total NPS-TP loads from the five main tributaries ranged from 10.6×10^6 kg to 60.0×10^6 kg from 2004 to 2017. Like the TP loads, the minimum NPS-TP loads appeared in 2016 while the maximum was in 2012. There was a big difference in yearly discharge (Figure 5(a)). The yearly discharge in 2012 was the second largest during the 14 years, while the yearly discharge in 2006 was the smallest. This indicated that both TP loads and NPS-TP loads will fluctuate greatly in the years with larger and smaller discharge, but discharge was not the only influencing factor.

The contribution rate of NPS-TP loads to total TP loads ranged from 25.4% to 67%, fluctuating around 50% from 2004 to 2017 (Figure 5(b)). The yearly average NPS-TP loads were 24.91×10^6 kg in the 14 years, accounting for 50.8% of yearly average total TP loads (Figure 5(b)). NPS pollution was an important factor affecting TP concentration in the mainstream of the upper Yangtze River. Regarding the treatment of TP in the upper reaches of the Yangtze River, both point source and NPS pollution should be considered.

Distribution characteristic of pollution loads

The tributaries' contributions to total TP loads and total NPS-TP loads were spatially heterogeneous (Table 4). The tributary contributions to total NPS-TP loads were ranked: Jinsha River, Jialing River, Wu River, Min River and Tuo River, and the tributary contributions to TP loads were ranked: Jinsha River, Min River, Wu River, Jialing River and Tuo River. This phenomenon was strongly related to the discharge of the tributaries. Monthly TP fluxes in every tributary were affected by both monthly TP concentration and monthly discharge. According to correlation analysis

Table 4 | Spatial distribution of average TP loads and average NPS-TP loads

	Pollution load of TP (10^6 kg)		
	Point source (10^6 kg)	Non-point source (10^6 kg)	Total (10^6 kg)
Jinsha River	8.40	8.10	16.49
Min River	8.38	4.12	12.50
Tuo River	1.16	1.56	2.72
Jialing River	1.23	6.73	8.00
Wu River	4.96	4.40	9.32
Total	24.1	24.9	49.0

of monthly TP fluxes with monthly TP concentration and monthly water discharge in every tributary, both monthly TP concentration and monthly average water discharge established a positive correlation with monthly TP fluxes (Figure S3). The correlation coefficient which was established by TP fluxes and water discharge was larger than that established by TP fluxes and TP concentration. This indicated that TP loads flowing into the mainstream from the tributaries were more associated with discharge than TP concentration. NPS-TP loads, which were transported by surface runoff, were also greatly affected by discharge. TP loads were mainly from the Jinsha and Min rivers, and TP loads from the two rivers accounted for 60% of total TP loads. NPS-TP loads were mainly from Jinsha River and Jialing River, and NPS-TP loads from the two rivers accounted for 59.1% of total NPS-TP loads. These phenomena were mainly due to the larger water discharge of the three rivers (Table 3). TP loads and NPS-TP loads from the Tuo River were the least, accounting for less than 10% of total loads. The reason was that the discharge of the Tuo River was lowest.

Monthly average TP loads and NPS -TP loads from 2004 to 2017 were calculated to analyze their temporal distribution characteristics (Figure 6). Both monthly NPS-TP loads and monthly TP loads changed simultaneously with discharge. The peak of TP loads and NPS-TP loads appeared in July and August, followed by June and September, which were the same as the discharge. NPS-TP loads of the four months were 17.7×10^6 kg, accounting for 71.2% of yearly average NPS-TP loads. TP loads of the four months were 30.1×10^6 kg, accounting for 62.7% of yearly average TP loads. These phenomena indicated the wet season was the peak period of inputting TP load and NPS-TP loads into the mainstream. In the wet season, 59% of TP loads flowing into the mainstream were from NPS pollution. TP loads and NPS-TP loads were least in the dry season (January, February, March, and December), accounting for 14.1% of yearly average TP loads and 6.9% of yearly average NPS-TP loads respectively. This was due to abundant precipitation happening in summer and the formation of surface runoff carrying surface pollutants into rivers, resulting in large NPS pollution loads in the wet season. The spatiotemporal distribution of TP loads and NPS-TP loads has similar laws, which further shows that NPS-TP loads have a great impact on the TP loads.

Contribution of non-point source in every tributary

The contribution of NPS-TP loads to TP loads was different in different tributaries (Table 4). The input TP load from Jialing River was mainly NPS, accounting for 84.5% of TP loads (Table 4). This was because 30% of the area of the Jialing River Basin was crop land (Han *et al.* 2016). The input NPS-TP loads from Wu River, Tuo River, and Jinsha River accounted for 47.2%, 57.4%, and 49.2% of their TP loads (Table 4), which indicated that both point source and NPS were important pollution sources of the three basins. Crop land was 80% of the area of Tuo River Basin and 30% of

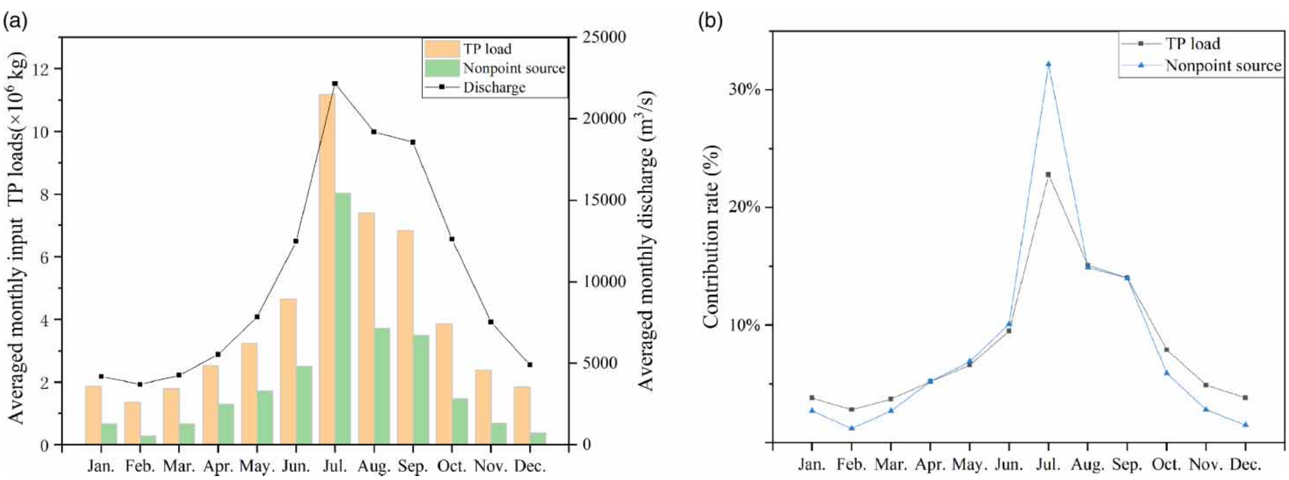

Figure 6 | Temporal distribution characteristics of TP loads and NPS-TP load.

the area of the Wu River Basin, and the Yunnan-Guizhou Plateau area, which was in the downstream of Jinsha River, was the concentration area of the crop land (Yang 2018). Large amounts of phosphate fertilizer resulted in serious NPS pollution in these areas. In terms of point source pollution, 15 phosphogypsum accumulation sites exist in Deyang City in the upper reaches of the Tuo River. In 2016, 533×10^4 t of phosphogypsum was produced, but the utilization rate was only 53% (Qin *et al.* 2018). In the Wu River Basin, 28 phosphate mining and chemical enterprises exist in Guizhou Province, resulting in a ten-year average TP concentration of 0.27 mg/L flowing into the mainstream from the Wu River (Qin *et al.* 2018). In the Jinsha River, there are many industrial and mining enterprises, which discharge more than 40 million tons of sewage water every year (Luo *et al.* 2007). In the Min River, the contribution rate of NPS-TP loads was only 33% (Table 4), and TP loads flowing into the mainstream were mainly from point source pollution. In the Min River Basin, a total of 31 major phosphate mining and phosphorus chemical enterprises exist with TP concentration reaching 0.76 mg/L at the sewage outlet (Qin *et al.* 2018).

Causes of variation in total phosphorus concentration and loads

The TP concentration in the mainstream was influenced by input TP loads from tributaries and a retention effect caused by TGR impoundment in June 2003 (Figure 7). TP retention in the mainstream was calculated by subtracting the outflow TP fluxes of Yichang station from the inflow TP fluxes of the five main tributaries. According to the correlation analysis of discharge-weighted TP concentration with input TP loads and TP retention, we find that both TP loads and TP retention were positively correlated with the TP concentration of the mainstream (Figure 7). The influence of TP retention on TP concentration may be related to the release of deposited phosphorus under the proper conditions. The correlation coefficients of discharge-weighted TP concentration with input TP loads and TP retention were 0.73 and 0.67, respectively (Figure 7). This indicated that input TP loads had a greater impact on the TP concentration than the retention effect. TP concentration of the mainstream was mainly influenced by input TP loads from tributaries.

TP loads fluctuated greatly in the years with larger and smaller discharge. This indicated that TP loads were affected by rapid discharge change. Furthermore, TP loads in the upper YRB were obviously related to economic development and intensity of pollution control. In the 1990s, the Yangtze River Economic Zone developed rapidly, but this was at the expense of massive resource consumption and the ecological environment. With economic development of the upper YRB, the Chinese government began to realize there were pollution problems caused by the economic

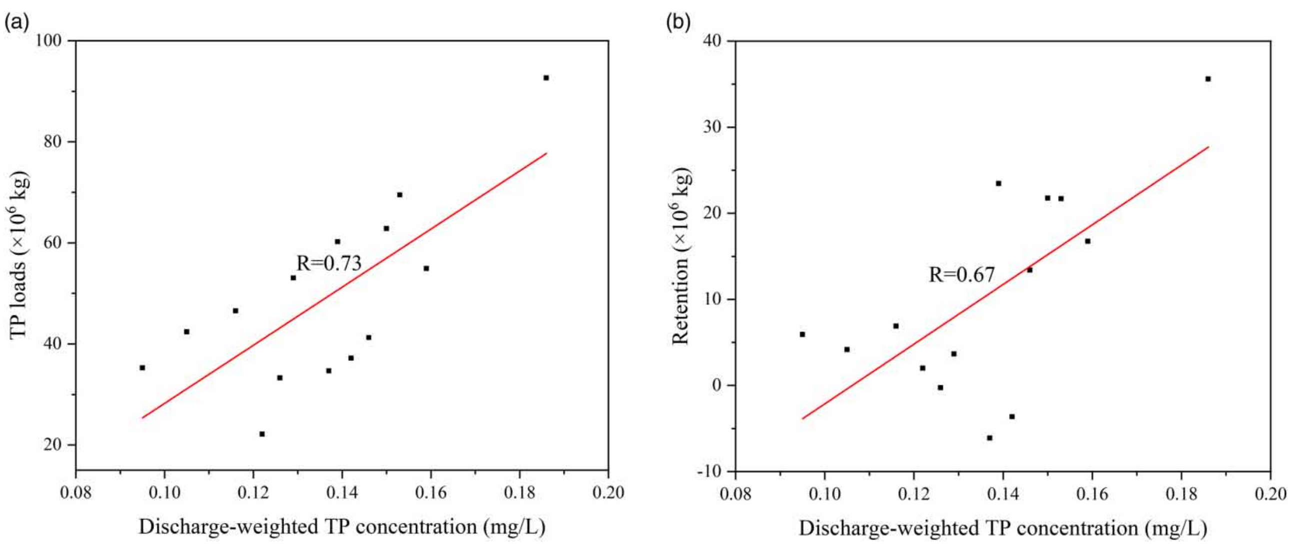

Figure 7 | Correlation analysis of (a) discharge-weighted TP concentration with input TP loads from five tributaries and (b) retention effect caused by TGR impoundment.

development and adopted a series of measures to protect the environment, such as the establishment of urban sewage treatment plants and the improvement of industrial waste water treatment rates. From 2004 to 2006, economic development was slower, the use of phosphorus fertilizer was less, and the discharge of waste water was stable (Figure 8). Increased investment in industrial pollution control (from 3.37×10^{10} yuan to 4.35×10^{10} yuan) combined with soil erosion control (from 1.19×10^7 hm^2 to 1.34×10^7 hm^2) reduced TP loads. Therefore, TP loads flowing into the mainstream decreased from 2004 to 2006 (Yang 2018).

From 2006 to 2012, the density of production and living has increased with sustained economic development. The use of phosphate fertilizers (from 72.7×10^7 kg to 79.5×10^7 kg) and the discharge of waste water (from 51.1×10^{10} kg to 66.2×10^{10} kg) have increased rapidly, but investment in industrial pollution control has only increased slightly, and even dropped in 2008–2010 (Figure 8). The treatment intensity was not able to meet the requirements, so TP loads rebounded from 2006 to 2012 (Yang 2018). The environmental pollution brought by rapid development approached the limit of the ecological environment, so the Chinese government intensified pollution treatment. From 2012 to 2014, funds for industrial pollution control increased rapidly (Figure 8). Industrial pollution control investment in 2014 was 2.1 times that of 2004. Despite the continued economic development and the increasing amount of waste water, TP loads from waste water, which belonged to point source pollution, had a drop of 60% from 2013 to 2017 because of effective waste water treatment (Figure 8). In terms of NPS pollution, the control area of soil erosion increased from 1.60×10^7 hm^2 to 1.96×10^7 hm^2 with an increase of 20.9%. The agricultural consumption of phosphate fertilizer had a drop of 5.0% from 79.50×10^7 kg in 2012 to 75.54×10^7 kg in 2017 (Figure 8). The control intensity of point source pollution was greater than that of NPS pollution from 2012 to 2017, so treatment of NPS pollution still presents great potential. After a series of point source and NPS pollution treatments, TP loads sharply decreased from 2012 to 2017. With such intensive treatment, TP loads were still decreasing despite the reduction in investment of industrial pollution after 2015. With the variation of TP loads from tributaries, TP concentration in the mainstream changed similarly.

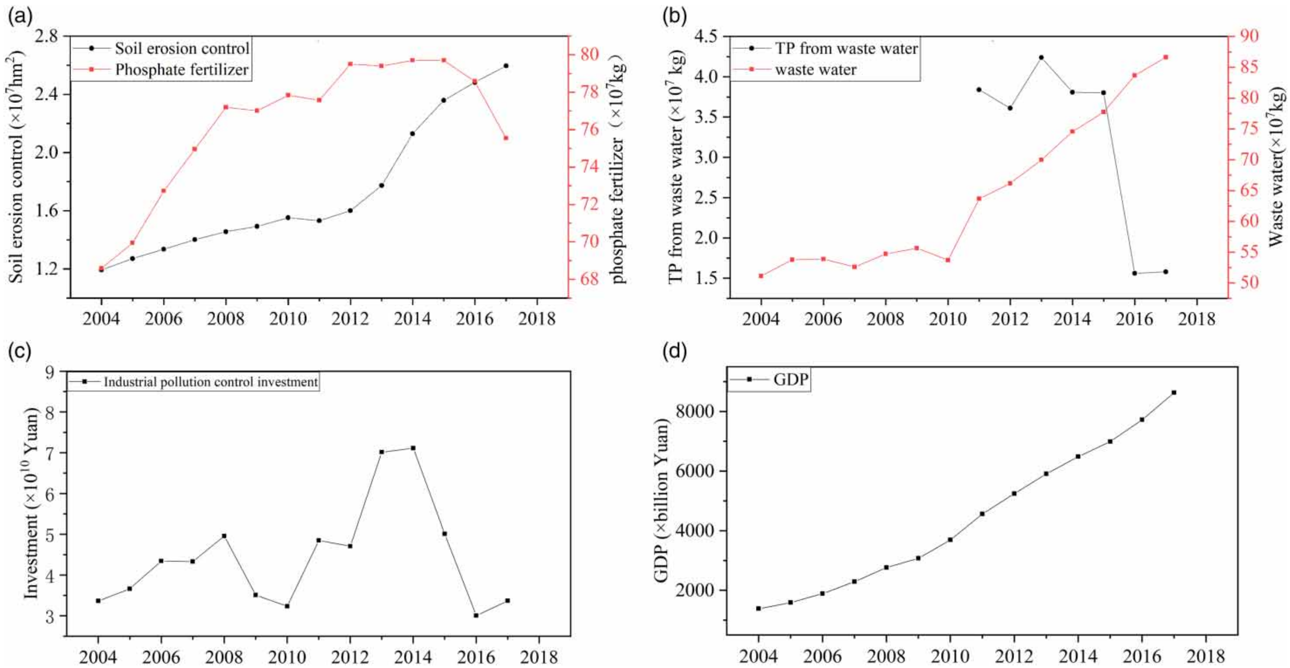

Figure 8 | (a) The control area of soil erosion and agricultural consumption of phosphate fertilizer; (b) waste water and TP from waste water; (c) industrial pollution control investment; (d) gross domestic product (GDP).

Implications for future water policy of the upper YRB

For the mainstream, TP concentration was mainly affected by inputted TP loads from the tributaries, therefore phosphorus pollution in the mainstream can be controlled by reducing pollution loads from tributaries. From 2004 to 2017, 50.8% of TP loads inputted by tributaries came from NPS pollution, indicating that comprehensive treatment of point source and NPS was essential in pollution control. In different tributaries, the contribution rate of NPS-TP loads into the mainstream was different, so it is necessary to set different control plans according to contributions of point source and NPS in different areas. It is worth noting that the control intensity of point source pollution was greater than that of NPS pollution from 2012 to 2017, so treatment of NPS pollution still presents great potential.

In the upper YRB, the most polluted areas were the Tuo River and Wu River, and the yearly average TP concentrations of the two rivers were worse than Grade III. Although TP concentrations of all the stations on the mainstream, including in the TGR, showed downward trends from 2013 to 2017, TP concentrations of most sites in the TGR area were beyond 0.05 mg/L, which means TP concentration in the TGR area did not meet the water quality management standard (Figure S4). Therefore, the critical control area of phosphorus pollution was in the Wu River Basin, Tuo River Basin and TGR area.

CONCLUSIONS

This study focused on phosphorus pollution in the upper YRB from 2004 to 2017. The TP concentrations in the mainstream and five main tributaries were analyzed, and TP loads and NPS-TP loads flowing into the mainstream from five tributaries were also estimated based on the base flow segmentation method.

The TP concentration in the mainstream showed a fluctuating trend of decreasing–increasing–decreasing from 2004 to 2017. Larger TP concentration was observed in the wet season from 2004 to 2017. Lower TP concentration occurred in the dry season from 2004 to 2012, but it was in the normal season from 2013 to 2017. TP concentration of tributaries showed great spatial heterogeneity, and the Wu River and Tuo River had higher TP concentration in recent years.

NPS was an important source of TP loads to the mainstream. Average NPS-TP load flowing into the mainstream from tributaries was 24.91×10^6 kg per year, accounting for 50.8% of the total yearly average TP load from 2004 to 2017.

NPS-TP loads mainly from Jinsha River and Jialing River accounted for 59.1% of NPS-TP loads and mainly occurred in the wet season, accounting for 71.2% of yearly average NPS-TP loads.

The TP concentration in the mainstream was affected by TP loads from tributaries and the retention effect caused by TGR impoundment, and TP loads from tributaries had a greater impact on the TP concentration than the retention effect. The long-term variation trend of TP loads from tributaries was mainly affected by economic development, intensity of pollution control and significant discharge change.

In the light of these regional differences, we recommend that key control areas of phosphorus pollution should be set in the Wu River Basin, Tuo River Basin, and the TGR area. In different tributaries, the contribution rate of NPS-TP loads to the TP loads was different, so it is necessary to set different control plans according to contributions of point source and NPS pollution in different areas.

AUTHOR CONTRIBUTIONS

Conceptualization, Q.L. and Z.Y.; methodology, Q.L. and Z.Y.; software, D.L. and Q.L.; validation, Z.Y., Y.Y. and D.L.; formal analysis, Q.L.; resources, Z.Y.; data curation, Q.L.; writing – original draft preparation, Q.L.; writing – review and editing, Q.L. Z.Y. Y.Y. H.Z.; visualization, D.L. Z.Y.; supervision, Z.Y.; funding acquisition, Z.Y. All authors have read and agreed to the published version of the manuscript.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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