



Article Simulation Study on the Effect of Non-Point Source Pollution on Water Quality in the Upper Reaches of the Lijiang River

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Abstract: Maintaining good water quality in the Lijiang River is a scientific and practical requirement for protecting and restoring the environmental and ecological value of the river. Understanding the influence of non-point source pollution on the water quality of the Lijiang River is important for water quality maintenance. In this study, the pollutant flux in the upper reaches of the Lijiang River was calculated based on water quality monitoring, non-point source pollution, and point source pollution statistics. The Z-Q relation curve method, hydrologic analogy method, and contour map method were used to estimate the flow of the Lijiang River. We then constructed a water quantity-water quality balance model of the upper reaches of the Lijiang River based on an equilibrium equation of water quantity and a modified one-dimensional steady-state model of the river. Water quality changes in the upper reaches were simulated for a wet, normal, and dry season. The simulation errors were all within -30% to 30%, which was in line with the pollution simulation requirements of the Standard for hydrological information and hydrological forecasting (GB/T 22482-2008). The simulated reliability of each water quality indicator is at a high level, based on the calculated Nash-Sutcliffe efficiency coefficient. The overall model simulation results were good. The simulation results show that the impact of non-point source pollution on the water quality of the upper reaches of the Lijiang River was greater than that of point source pollution. The effect of different types of non-point source pollution on the water quality of the Lijiang River was as follows: rural domestic pollution > urban household pollution without centralized treatment > pollution from agricultural cultivation. This study provides technical support for the long-term hydrology and water quality monitoring of the Lijiang River and provides a basis for the reduction in non-point source pollution and the continuous improvement of the water quality in the Lijiang River Basin.

Keywords: upstream of the Lijiang River; non-point source pollution; water quantity and quality; model simulation

1. Introduction

Non-point source pollution is the main source of pollution affecting water quality in rivers [1–3] and an important factor in the eutrophication of water bodies [4–6]. As the "mother river" of Guilin, the Lijiang River shoulders the heavy responsibility of water consumption for industry, agriculture, domestic use, and the environment [7]. In recent years, with the implementation of a series of environmental governance measures, the overall water quality of the Lijiang River basin is good, but there are also some tributaries in some periods of poor water quality problems [8]. The quantitative calculation of the impact of different pollution sources on the water quality of the Lijiang River is of great



Citation: Li, Z.; Dai, J.; Li, Z.; Liu, Y.; Xu, J.; Zhang, Z.; Xu, B. Simulation Study on the Effect of Non-Point Source Pollution on Water Quality in the Upper Reaches of the Lijiang River. *Water* **2022**, *14*, 3995. https:// doi.org/10.3390/w14243995

Academic Editor: Liudmila S. Shirokova

Received: 18 October 2022 Accepted: 5 December 2022 Published: 7 December 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). significance for accurately putting forward the countermeasures for the water environment management of the Lijiang River.

As a karst area, the Lijiang River Basin is particularly susceptible to the influence of pollutants due to its unique karst geological characteristics. The special karst land-form leads to non-point source pollution entering the groundwater system, along with the runoff, which poses challenges in the prevention and control of water pollution [7]. Planting land (paddy and dryland), urban construction land, and rural residential land for human production and living all produce pollution sources. The main land use types, including woodland, grassland, and industrial and construction land, also produce pollutants such as nitrogen and phosphorus [9]. The small-scale livestock farming has the characteristics of dispersion and randomness, which makes it difficult to make an accurate statistical estimation. Improving water quality requires understanding pollution sources and pollutant transport processes. Pollutant transport calculations affect the accuracy of the environment regulation decisions for aquatic environments [10]. Many researchers have used simulations of non-point source pollution in watersheds. The Soil and Water Assessment Tool (SWAT) model has been used to simulate transport processes and the discharge of pollutants to a watershed outlet [11-13]. By constructing a Best Management Practice (BMP) optimal allocation scheme at different spatial scales, water quality improvement can be maximized [14]. The Hydrological Simulation Program-Fortran (HSPF) model and regression model were applied to the Luan River Basin to estimate the load of non-point source pollutants [15]. By combining the pollution load module with the Hydro-Informatic Modeling System (HIMS), we simulated the process of pollution generation and transport in semi-arid and sub-humid areas and quantified the pollutant load [16]. The Dynamic Export Coefficient Model (DECM) was used to simulate non-point source pollution in the catchment and to quantify the effect of different underlying surfaces on effluent coefficients [17]. Using a combination of the Eulerian–Lagrangian Alternating Direction Implicit Method (ELADI) and Water Quality Analysis Simulation Program (WASP) models, we constructed a two-dimensional water environment model with orthogonal curves to simulate and analyze the dynamic response relationship between the pollutant load and water quality in the lower reaches of the Ganjiang River [18]. The pollutant loads at the watershed outlet were estimated by simulating rainfall, runoff, and non-point source processes [19]. The Source-precipitation-landscape Model (SPLM) was used to simulate the total nitrogen pollution output of non-point sources in the Haihe River basin. The results showed that rural domestic pollution and the agricultural industry contributed the most to the total nitrogen emission [20]. The Water Quality Index (WQI) was used to assess the state of the water quality of the Turnasuyu Stream, and multivariate statistical analysis was conducted to assess the impact of agricultural activities and domestic pollution on the water quality in the Turnasuyu Basin [21]. Artificial Neural Network (ANN) models can be used to predict the water quality of rivers, lakes, reservoirs, ponds and streams by capturing the relationships between water quality data [22–24]. With ammonia nitrogen, total phosphorus, and chemical oxygen demand as pollution indicators, the Hydrodynamic Water Environment Model was used to predict the response of sewage under different scenarios of agricultural and urban non-point source pollution control and to evaluate the effectiveness of the different scenarios [25]. The general water quality model is powerful; however, it requires a large number of parameters and is not highly adaptable to the complex water system in the study area.

In this study, the water quality and pollution sources in the Lijiang River Basin were investigated and analyzed, providing a basis for the reduction in non-point source pollution and the continuous improvement of the water quality in the Lijiang River Basin, as well as technical support for long-term hydrological and water quality monitoring of the Lijiang River, in the future, in order to provide management countermeasures for protection of the water environment, water pollution prevention, and pollution source control of the urban sections of the Lijiang River. As conditions such as hydrogeological conditions and soil types vary from region to region, the values used in this study were set within a reasonable range, and the model simulations achieved the desired results. The remainder of this paper is organized as follows. Section 2 introduces the general situation of the study area and the main data sources. We determine the intersection of the main and tributary streams and the calculation nodes according to the distribution of the upper Lijiang River water system and the distribution of the hydrological and water quality sections, we modify a one-dimensional steady-state model, and establish a water quantity-water quality balance model. Section 3 presents the validation of the water quantity-water quality balance model, the simulation of the water quality indicator concentrations during the wet, normal, and dry seasons, and the simulation of scenarios of pollution discharges from point sources and different types of non-point sources. Section 4 discusses and summarizes the contributions of point source pollution and non-point source pollution and their influences on the water quality of the Lijiang River. In addition, the extent of the impacts of the different non-point source pollution sources on the water quality are analyzed and compared. Finally, the limitations of this study are analyzed and discussed, and future research is proposed.

2. Materials and Methods

The workflow of this study is shown in Figure 1. First, sub-watershed delineation was carried out and detailed information and data were collected and collated. Second, the amount of pollution entering the river and nodal divisions were calculated and a water quantity-water quality balance model was constructed. Finally, model validation and pollution source simulation were carried out for analysis and comparison.

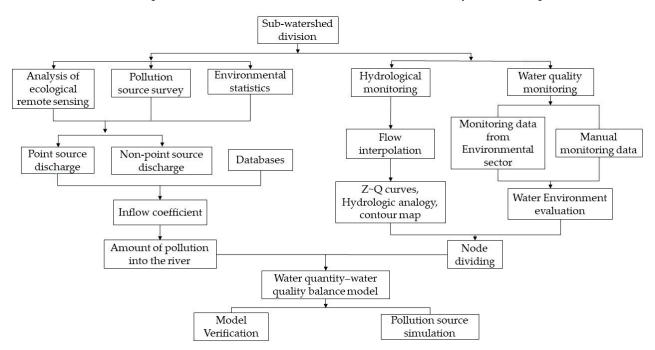


Figure 1. Workflow of this study.

2.1. Overview of the Study Area

The Lijiang River originates in Mao'er Mountain (altitude 2141.5 m), the main peak of the Yuecheng Mountain in the northwest of Xing'an County, Guilin City. The main stream of the Lijiang River flows through Xing'an, Lingchuan, Guilin, Yangshuo, Pingle, and other cities and counties, with a total length of 214 km [26]. The Lijiang River is a rain source river with an annual average runoff of 4.031 billion m³. The wet season runs from April to August and the dry season runs from December to the end of January of the next year [8]. Guilin has less arable land per capita, and the quality of the arable land needs to be improved. The arable land per capita is 0.085 hm², which is lower than the 0.096 hm² in the region and 0.106 hm² in the country. The extent and effectiveness of the land use and the level of intensive land use in Guilin are not high, and the land is heavily used rather than

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maintained, with local soil erosion being more severe. The agricultural planting pollution is extensive, complex, and random, rendering statistical analysis somewhat difficult. In the Lijiang River Basin (urban areas), the watershed surface contains 150 enterprises with industrial sewage discharge, of which the sewage from 46 of these enterprises did not enter the sewage treatment plant. For the industrial enterprises that did not utilize the sewage treatment plant, their sewage was mainly discharged directly into the river and lake water bodies, agricultural land, ground seepage evaporation, and so on. The number of households for which the rural domestic sewage enters the rural centralized treatment facilities and the number of households for which the sewage enters a municipal pipe network accounted for 23.8% of the total. The remainder of the rural household sewage was discharged directly into farmland and local water bodies. The study area includes the Guilin urban section of the Lijiang River as well as areas upstream and downstream. The upstream reach includes Rongjiang Town, Xing'an County (Dabutou section). The downstream reach includes Caoping Town, Yangshuo County. The water quality monitoring point is in the Mopan Mountain section. From the water quality monitoring section of Dabutou to the section of Mopan Mountain, the total length is approximately 60 km. The main tributaries include the Gantang River, Taohua River, Xiaodong River, Nanxi River, Xiangsi River, Huajiang River, and Chaotian River [27]. The total study area is 2759.78 km² and includes 11 sub-basins, as shown in Figure 2.

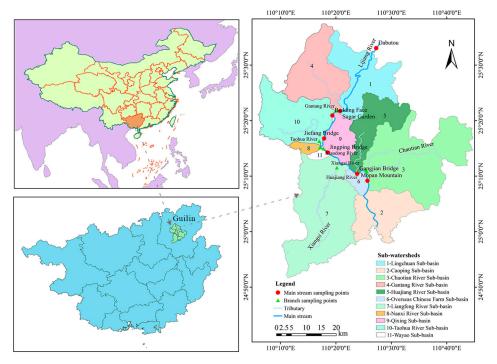


Figure 2. Research area and sub-watersheds.

2.2. Pollutant Transport Calculation Unit and Node Division

The computing units in the tributaries of the upper reaches of the Lijiang River correspond to the sub-basins, and the computing nodes are located at the outlet of the sub-basins. The computing node located at the outlet of the sub-basin controls the pollution load discharge of the sub-basin (Figure 2). In order to better match the sub-watershed with the water quality calculation node, the Taohua River basin, Qixing basin, and Overseas Chinese Farm basin were subdivided as part of the calculation.

Seven main stream computing nodes and six intervals were selected from existing monitoring points established by states, districts, and municipalities and the new monitoring points in this study. The upstream-to-downstream section nodes were: Dabutou (municipal), Sugar Garden, Bedding Face (municipal), Jiefang Bridge, Jingping Bridge, Gangjian Bridge, and Mopan Mountain (district). The tributary nodes were set at the outlet of major tributaries, including the Gangtan River, Taohua River (municipal), Nanxi River (municipal), Xiaodong River (municipal), Wayao River, Liangfeng River, Huajiang River, Jiansha River, and Chaotian River. The pollution load calculation units, nodes division, and interval distances in the study area are shown in Table 1. The water quantity and water quality were measured at each monitoring point. Field sampling was carried out with reference to *The Technical Specification for Surface Water and Sewage Monitoring* (HJ/T 91-2002) [28], using a Plexiglas water sampler to collect mixed water samples directly from river sections at different depths. The samples were stored in rinsed 1000 mL brown glass bottles. The parameters recorded at each site included the flow velocity, water level, water temperature, pH, and dissolved oxygen content. The cross section was measured using a dipstick. Furthermore, water level buoy methods and a handheld electro wave radar velocity meter (Stalker II SVR) were used to determine the flow velocity. An ultrasonic sounder or tower gauge was used to determine the water depth and channel geometry, a portable dissolved oxygen meter was used to determine the dissolved oxygen content, and a portable pH meter was used to determine the pH. The water samples collected on the same day were stored in the laboratory at a low temperature of 0-4 °C, and the samples were processed and analyzed within 24–48 h of collection. The water quality indexes determined were the total nitrogen (TN), ammonia nitrogen (NH₃-N), and chemical oxygen demand (COD). Referring to The Analytical Methods for Water and Wastewater Monitoring [29], the TN of the Alkaline potassium persulfate digestion UV spectrophotometric method (HJ 636-2012), the NH $_3$ -N was determined using the Nessler's reagent colorimetric method (HJ 535-2009), and the COD was determined using the potassium dichromate method (GB 11914-89). The monitoring period was between October 2019 and October 2020. The monitoring frequency was once a month.

Table 1. Calculation unit, main stream, and tributary.	

Area Unit	Main Stream Node Interval	Interval Distance/km	The Inflow of Major Tributaries
Lingchuan Sub-basin	Dabutou-Sugar Garden	31.5	/
Gantang River Sub-basin	Sugar Garden -Bedding Face	1.8	Gantang River
Qixing Sub-basin1, Taohua River Sub-basin2	Bedding Face-Jiefang Bridge	9.0	/
Taohua River Sub-basin1, Nanxi River Sub-basin Wayao Sub-basin, Qixing Sub-basin2	Jiefang Bridge-Jingping Bridge	6.0	Taohua River, Nanxi River, Xiaodong River
Liangfeng River Sub-basin, Qixing Sub-basin3 Overseas Chinese Farm Sub-basin1	Jingping Bridge-Gangjian Bridge	12.3	Liangfeng River
Huajiang River Sub-basin, Chaotian River Sub-basin Overseas Chinese Farm Sub-basin2	Gangjian Bridge-Mopan Mountain	6.4	Hua River, Chaotian River, Jiansha River

2.3. Establishment of Water Quantity–Water Quality Balance Model

According to the point source pollution and non-point source pollution emissions from the second pollution source census [30], as well as the latitude and longitude coordinates of each enterprise in the pollution census statistics, the location information of industrial pollution emissions was converted into a point vector file using the ArcGIS software. Then, the overlay analyses of other factors (e.g., basin and basin boundary) and the basin boundary segmentation analysis were carried out on the file.

The distribution of industry, livestock industry, and pollutant emissions in each subwatershed was calculated using segmentation, screening, and statistical analysis for each sub-watershed as a unit. The urban domestic pollution production in each sub-watershed was calculated using the environmental statistics of urban per capita annual domestic pollution emissions in Guilin city, combined with the population of each sub-watershed. According to closed tests by Guilin Drainage Company in 2020, only 73.4% of the domestic sewage enters the sewage treatment plant through the urban pipe network. This means that 26.6% of the domestic sewage is discharged as pollution. From this information, we calculated the pollutant discharge of each sub-basin. The output coefficient method was used to calculate the non-point source pollution of agricultural crops and the emission of land use pollutants. The pollution statistics for the administrative region were transformed into the pollution statistics of the sub-watershed. Using these pollution statistics and water quantity and quality data, a water quantity–water quality balance model was constructed.

2.3.1. Equilibrium Equation for Water Quantity

Without considering the effect of evaporation, the equilibrium equation of water quantity of the upper and lower reaches of the main stream of the Lijiang River can be expressed as:

$$Q_B = Q_A + \sum_{1}^{n} Q_t + Q_s + Q_g - Q_l$$
(1)

where Q_A is the flow of upstream node A, m³/s; Q_B is the flow of downstream node B, m³/s; $\sum_{l}^{n} Q_l$ is the inflow of tributaries between A and B, m³/s; Q_s is the replenishment amount of surface runoff entering from A to B, m³/s; Q_g is the supply amount of underground runoff entering from A to B, m³/s; and Q_l is the flow rate of leakage from A to B into a river bed, karst cave, or underground crack, m³/s.

2.3.2. Equation for Pollutant Flux Calculation

The pollutant flux of the river section is the product of discharge, pollutant concentration and time:

$$W = Q \times C \times T \tag{2}$$

where *W* is the pollutant flux in the river section, ton; *Q* is the average monthly discharge of the river section, m^3/s ; *C* is the monthly average concentration of pollutants in the river section, mg/L; and *T* is time (a month is calculated as 30 days) *T* = 2,592,000 s.

2.3.3. Modified One-Dimensional Steady-State Model

A modified one-dimensional steady-state model was used to simulate the transport of pollutants between sections (nodes) of the main stream of the Lijiang River. A onedimensional steady-state model of rivers can be expressed as:

$$C = C_0 \times \exp\left[-(K) \times \frac{x}{86,400u}\right]$$
(3)

where *C* is the pollutant concentration of the calculated section, mg/L; *C*₀ is the pollutant concentration of the initial section, mg/L; *K* is the synthetic attenuation coefficient, 1/d; *u* is river velocity, m/s; and *x* is the reduction distance from the initial section to the downstream computed section, m.

The pollution abatement capacity of a river (e_1) is related to the comprehensive attenuation coefficient *K*, the abatement distance *x*, and the flow rate *u*, and is calculated as follows:

$$e_1 = \exp\left[-(K) \times \frac{x}{86,400u}\right] \tag{4}$$

In this study, water and pollutants in each sub-watershed entered the main stream of the Lijiang River through tributaries. However, under heavy rainfall conditions, runoff and pollutants also enter the main stream via sheet flow from both sides. Underground runoff recharge and riverbed leakage also occur along the course, providing opportunity for pollutants enter or flow out of the main stream [31]. Therefore, when a one-dimensional steady-state model is applied in this study, the reduction distance of pollutants is generalized, and the average reduction distance is considered to be half of the distance between main flow nodes (sections), or 0.5x. The combined pollutant reduction capacity (e_2) of the

tributary inflow, surface runoff recharge, underground runoff recharge, and leakage loss can be calculated as:

$$e_2 = \exp\left[-(K) \times \frac{0.5x}{86,400u}\right]$$
 (5)

2.3.4. Water Quantity–Water Quality Balance Model

In the water quantity balance Equation (1), both sides are multiplied by pollutant concentration *C* and time *T*. The pollutant concentration imported into point A and interval (A–B) was reduced according to the modified one-dimensional steady-state model. The established water-quality balance model is expressed as:

$$Q_B \times C_B \times T = (Q_A \times C_A)e_1 \times T + (\sum_{1}^{n} Q_t \times C_t + Q_s \times C_s + Q_g \times C_g + W_e - Q_l \times C_l)e_2 \times T$$
(6)

where C_B is the pollutant concentration of the downstream node (section) B, mg/L; C_A is the pollutant concentration of the upstream node (section) A, mg/L; C_t is the concentration of pollutants in tributaries that enter between A and B, mg/L; C_s is the base concentration of pollutants replenished by surface runoff when there is no exogenous pollution discharge, mg/L; C_g is the base concentration of pollutants replenished by runoff when there is no exogenous pollution discharge, mg/L; and C_l is the pollutant concentration of leakage between A and B, mg/L.

According to the equation for pollutant flux (2), Equation (6) can be expressed as:

$$W_B = W_A \times e_1 + \left(\sum_{1}^{n} W_t + W_s + W_g + W_e - W_l\right) e_2 \tag{7}$$

where W_e in Equations (6) and (7) represents the monthly amount of point and non-point source pollution into the river within the interval *AB* (the calculation time here is in months).

2.4. Source and Calculation of Model Parameters

- 2.4.1. Concentration and Discharge of Pollutants in Main Stream and Tributaries
- Pollutant concentration

The pollutant concentrations for the main stream of the Lijiang River were obtained from measured data at Dabutou, Sugar Garden, Bedding face, Jiefang Bridge, Jingping Bridge, Gangjian Bridge and Mopan Mountain. The concentration of pollutants in the tributaries of the Gangtan River, Taohua River, Nanxi River, Xiaodong River, Wayao River, Liangfeng River, Huajiang River, Jiansha River and Chaotian River were measured data from this study.

- Water flow data collection and calculation
- 1. Flow data collection

In this study, we collected data on water level, discharge, and water quality in the Dabutou section and Guilin Hydrological station. We collected water level and water quality data in the Bedding face section and Mopan Mountain section. In the main stream section, the Z–Q curve of the Darong River (Dabutou) was established to obtain the corresponding fitting equation. The Z–Q curves of the Chaotian River, Daxu (Jiansha River), Liangfeng River (Xiangsi River), Nanxi River, Huajiang River, and Taohua River were established in the tributary section to obtain their fitting equations. Some sections along the Z–Q curves needed to be appropriately extended with high and low water, so the corresponding high and low water extension lines should be made to improve the fitting degree of different water periods.

2. Flow calculation

To calculate flow for sections without measured values, we used the water level flow (Z–Q) relation curve method [32], hydrologic analogy method (distance interpolation

method) [33], contour map method [34], and other methods, depending on what data was available (Table 2).

Table 2. Flow interpolation method for main stream and tributary nodes.

	Node	Method		Node	Method
Main stream	Dabutou	Z–Q curves		Gantang river	Hydrologic analogy method
	Sanjie	Z–Q curves		Taohua river	Z–Q curves
	Gantan pontoon bridge	Hydrologic analogy method, contour map method Hydrologic analogy method, contour map method Hydrologic analogy method, contour map method	Tributary	Nanxi river	Z–Q curves
	Bedding face			Xiaodong river	Hydrologic analogy method
	Jiefang bridge			Liangfeng river	Z–Q curves
	Jingping bridge	Measured data from Guilin hydrologic Station		Huajiang river	Z–Q curves
	Gangjian bridge	hydrologic analogy method, contour map method		Jiansha river	Z–Q curves
	Mopan Mountain	Hydrologic analogy method, contour map method		Chaotian river	Z–Q curves

2.4.2. River Leakage and Pollutant Concentration

The average leakage rate in the middle and lower reaches of the Lijiang River is approximately 12% [35]. Due to the differences in the riverbed properties and karst development, the leakage rate of different sections varies. Using the research results and taking into consideration the influence of karst development and other factors on the leakage amount, this study estimated the leakage amount for each section. We then generalized the leakage concentration of pollutants in the river by taking the average value of the upper and lower sections.

2.4.3. Base Value of Runoff Recharge and Pollution Concentration

Using the equilibrium equation of water quantity, the total runoff recharge was calculated by subtracting the flow at point A, tributary inflow, and seepage from the flow at point B of the main stream. The runoff replenishment was divided into surface runoff replenishment and underground runoff replenishment (underground runoff is also called base flow). The runoff segmentation of the Qingshitan Reservoir in the Lijiang River Basin showed that the base flow index was 15–34% [36]. Based on this study, we allocated the total runoff volume in the study area to 80% of surface runoff and 20% underground runoff. Using the section from Dabutou to Sugar Garden as an example, there is a low amount of karst in the reach from Dabutou to sugar Garden, the leakage rate is 3% of the average flow of Dabutou and Sugar Garden reaches, the runoff recharge is the flow of Sugar Garden section minus the flow of Dabutou section plus the leakage, and the total runoff recharge is divided into 80% surface runoff and 20% underground runoff (Table 3).

Table 3. Water balance parameters from DaButou to Sugar Garden (in $m^3 \cdot s^{-1}$).

Water Period	Dabutou	Sugar Garden	Leakage	Total Runoff Recharge	Surface Runoff Recharge	Underground Runoff Recharge
Wet season	104.33	183.80	4.32	83.79	67.03	16.76
Normal season	20.75	59.17	1.20	39.63	31.70	7.93
Dry season	7.79	21.47	0.44	14.12	11.30	2.82

In their natural state, without the influence of human activities, soil and groundwater already contain a certain amount of nitrogen and phosphorus [37]. For this study, a base value of nitrogen and phosphorus was assigned to the runoff water recharging to the Lijiang

River. This base value in the surface runoff was based on the pollutant concentration in the month with the best water quality. The base value in the underground runoff was based on the Class II groundwater standard. Appropriate adjustments were made according to the simulation results.

2.4.4. Point and Non-Point Source Pollution Loads into the River

The load of point and non-point source pollution into the river between two main stream cross-sections (nodes) was equal to the sum of the pollutant load into the river of the corresponding sub-basin in the interval. For example, the pollutant load into the river between Dabutou and Sugar Garden cross-sections was the pollutant load into the river in the Lingchuan sub-basin. The pollutant load into the river from Damian to Jiefang Bridge was the sum of the pollutant load into the river from the two sub-basins of Qixing District Sub-basin 1 and Taohuajiang Sub-basin 2.

3. Results and Analysis

3.1. Model Verification

The water quality and flow data of the Lijiang River's multiple cross-sections between October 2019 and October 2020 were used to validate the water quantity–water quality balance model constructed in this study. In order to reduce the influence of accidental errors, the above period was divided into three seasons: wet, normal, and dry. The monthly average concentrations and average flow rates were used as simulation calculations for each season. Using NH₃-N concentration as an example, the simulation results are shown in Figure 3.

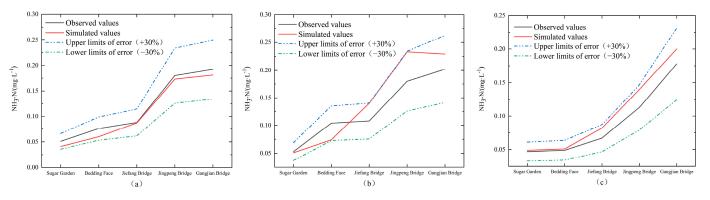


Figure 3. Comparison of measured and simulated values of NH₃-N concentration and error range during the (**a**) wet season, (**b**) normal season, and (**c**) dry season.

According to the *Standard for hydrological information and hydrological forecasting* (GB/T 22482-2008), the allowable error of water quality simulation is $\pm 30\%$ of the measured value. As Figure 3, it can be seen that the NH₃-N concentration simulation errors for each monitoring point are between -30% and 30%. This indicates that the model successfully simulates the NH₃-N concentrations. The other indicators are also in line with this range based on the calculated Nash–Sutcliffe efficiency coefficient (NSE) [38,39], that is, the NSE range of the NH₃-N of each computed node is 0.586–0.912, with an average value of 0.737. The NSE of the COD ranges between 0.622 and 0.818, with an average value of 0.470. Based on the calculated NES values, the NSE values of the COD and NH₃-N are closer to 1 and are comparable to those of other models (Table 4); this indicates that the model has credibility.

Model	Value	Reference
HSPF	>0.80	Donigian et al. [41]
APEX	>0.40	Ramanarayanan et al. [42]
DHM	>0.75	Motovilov et al. [43]
SWAT	>0.50	Santhi et al. [44]
SWAT and HSPF	>0.65	Singh et al. [45]

Table 4. Reported NSE values of different hydrological models (adapted by Moriasi et al. [40]).

3.2. Scenario Simulation

The constructed water quantity–water quality balance model was applied to simulate the impact of point source and non-point source pollution discharge on the water quality of the Lijiang River. Using the concentration of NH₃-N in the dry season as an example, six scenarios of changes in the point source discharge concentrations ($\pm 25\%$, $\pm 50\%$, and $\pm 75\%$) were used to calculate the associated NH₃-N concentrations in the Li-jiang River crosssection/node (Figure 4). The non-point source pollution in the Lijiang River basin includes agricultural cultivation, rural development, and urban development without centralized treatment. Using the NH₃-N concentration in the dry season as an example, six scenarios of change in agricultural pollution emissions ($\pm 25\%$, $\pm 50\%$, and $\pm 75\%$) were used to calculate the associated NH₃-N concentrations in the section/node of the Lijiang River (Figure 4).

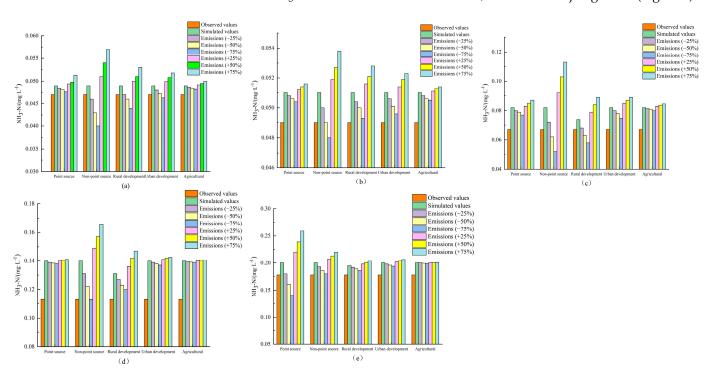


Figure 4. Variations in NH₃-N concentrations in the Lijiang River cross-section/node at (**a**) Sugar Garden, (**b**) Bedding Face, (**c**) Jiefang Bridge, (**d**) Jingping Bridge, and (**e**) Gangjian Bridge.

There are three urban sewage treatment plants in the Jingping Bridge–Gangjian Bridge section, resulting in a high proportion of point source pollution and abnormal simulated data. The simulation results presented in Figure 4 show that, with the exception of the Gangjian Bridge section, the water quality fluctuates significantly in response to changes in non-point source pollution emissions. The impact of non-point source pollution on the water quality of the Lijiang River is greater than that of point source pollution. The simulation results show that changes in the discharge of different types of non-point source pollution result in fluctuations in the water quality in all sections in the study area. The degree of impact of different types of non-point source pollution is: Rural development > Urban development without centralized treatment > Agricultural cultivation.

4. Discussion and Conclusions

The special topography, geological structure, karst distribution, and groundwater burial characteristics in the Lijiang River Basin (urban area) affect the migration of pollutants and the number of pollutants into the river to different degrees. The influence of the topography and geomorphology on the inflow coefficient is mainly reflected in the influence of the different slopes on the runoff process. In areas such as valleys and basins with steeper topographic slopes, the amount of surface runoff from rainfall that flows into the nearby river network is higher than in the plain areas. Areas with a high degree of karst development contain drop caves, caves, and underground rivers, for example, the number of caves found in the eastern part of Lijiang River is 223, with a density of 5.58 caves/km², and the area of the underground caves accounts for 43.93% of the total area. The special karst topography causes non-point source pollution to enter the groundwater system with the runoff, which in turn leads to a reduction of the amount of non-point source pollution discharged that directly enters the river. In areas with shallow groundwater depths, the amount of surface runoff recharging the groundwater is smaller, the amount of surface runoff entering the nearby river network is relatively high, and the amount of pollution entering the river is relatively high. In areas with deeper groundwater depths, the surface runoff infiltrates into the ground and recharges the groundwater in the process of flowing into the river network, which in turn leads to surface source pollution entering the groundwater, and the amount of pollution entering the river is relatively small.

According to long-term water quality monitoring, the pollutant concentrations and loads were found to be significantly different in the wet, normal, and dry periods. In the different seasons, the concentrations of each indicator were dry season > normal season > wet season, and the loadings were wet season > normal season > dry season. Due to the large flow in the wet season, the dilution effect of the river was also large, and the pollutant reduction capacity along the river was strong; therefore, the concentration was low in the wet season. The concentration was slightly higher in the normal season and was higher in the dry season. This is consistent with the results of previous studies [46,47]. The water quality was relatively stable and fluctuated little during the dry season. The water quality fluctuated greatly during the wet season due to heavy rain-fall and flood peaks. In fact, the amount of non-point source pollution entering the river was greatly affected by rainfall and runoff, and in the months with greater rain-fall, the amount of non-point source pollution entering the river was also large pollution was higher in the dry season than in the dry season.

The analysis results of the pollution sources show that, based on the emission statistics of the pollution discharge, the proportions of non-point source pollution for each of the pollution indicators were 89.99% for COD, 84.18% for NH₃-N, and 78.64% for TN. The non-point source pollution in the Lijiang River Basin accounted for approximately 85% of the total emissions, indicating that the non-point source pollution was the main source of pollution in the Lijiang River Basin. The major non-point sources of pollution were rural development pollution, agricultural planting pollution, urban development without centralized treatment, and so on. The contribution of the industrial sources to the pollution load of the Lijiang River Basin was relatively small. In terms of the emissions per unit area, the emissions per unit area of the rural and urban living were much higher than that of agricultural cultivation, and the pollution emissions were more concentrated. The emissions per unit area of the rural domestic pollution were greater than those of the urban domestic pollution, primarily because of the high rate of collection and treatment of urban domestic sewage and the low rate of decentralized discharge and centralized treatment of rural domestic sewage. This is consistent with the results of other studies. Cheng et al. [21] found that agricultural cultivation, rural domestic pollution, and animal husbandry were the top three sources of pollution impacting the river water quality. Zhang et al. [48] found that the river water quality in the LP area in the Minjiang River Basin was mainly affected by non-point source pollution from agricultural activities and domestic pollution,

and that fertilizer application strategies and livestock rearing management need to be optimized and advanced technologies developed to reduce rural septic tank and domestic pollution discharges.

The constructed water quantity–water quality balance model integrated the equilibrium equation of water quantity and the pollutant flux calculation equation and improved the one-dimensional steady-state model to calculate the influence of the emission changes of different pollution sources on the pollutant flux and concentration at downstream nodes. The simulation of water quality changes in wet, normal, and dry seasons for the upper node of the Lijiang River basin resulted in simulation errors between -30% and 30%. The overall simulation results were good. The simulation results for different emission scenarios of point and non-point sources showed that the water quality of all sections fluctuated substantially with changes in pollution emissions, with the exception of the Gangjian Bridge section. The impact of non-point source pollution on the water quality of the Lijiang River was greater than that of point source pollution. The degree of impact of different types of surface source pollution was: Rural development > Urban development without centralized treatment > Agriculture. Zhang et al. [49] found that the non-point source pollutants in Luoyang, Henan Province, had an impact on the water quality in the following order: agricultural planting pollution > rural domes-tic pollution > livestock manure pollution. As Henan is a major agricultural planting province, agricultural fertilization may be the most serious source of non-point source pollution.

The simulation accuracy of the water quantity–water quality balance model constructed in this study was good. However, there were some errors, which were caused by the aspects listed below. These sources of error must be improved upon in future research.

- The error in representing the monthly average by substituting it with the daily monitoring value during the actual monitoring of water quality;
- The error in the allocation of total pollutant emission statistics to individual months;
- The error caused by the linear distribution of the total discharge of non-point source pollutants to the periods of wet, normal, and dry water;
- The error caused by the model's insufficient consideration of pollutant transport and transformation mechanisms in rivers.

Under the current water quality conditions, environment management measures for the Lijiang River water should focus on the prevention and control of non-point source pollution. Comprehensive management should be conducted according to the basin conditions, pollutants, industries, types of pollution sources, and seasons. Water quality and quantity should be considered to inform integrated management. The construction of urban sewage treatment plants should be further improved, sewage networks and rural sewage treatment facilities should be constructed to increase the collection rate of domestic and industrial sewage, and the occurrence of such phenomena as direct discharge of sewage without treatment should be avoided. We suggest that the supervision and management of rural sewage treatment facilities be strengthened, with regular verification and assessment of the capacity of most sewage treatment stations, as far as possible, and real-time or regular monitoring of the quality of tailwater discharge. In future research, regular or online monitoring should be conducted to differentiate the data of the discharge destination, water quality index, and discharge from each pollution source in order to further improve the accuracy of the statistical data. We suggest that real-time monitoring equipment for hydrological and water quality indicators be added to accurately monitor the monthly average values, or even daily average values, to avoid such errors. Monitoring the changes in pollutant concentrations during rainfall can be considered in future studies to obtain data on pollution caused by rainfall and to facilitate a more comprehensive analysis of pollution transport and transformation mechanisms.

Author Contributions: Methodology, Z.L. (Zitao Li) and J.D.; investigation, Z.L. (Zitao Li), Z.L. (Zhangnan Li) and Z.Z.; resources, J.D. and Y.L.; data curation, Z.L. (Zitao Li), J.X. and B.X.; writing, original draft preparation, Z.L. (Zitao Li); writing, review and editing, J.D. and Y.L.; supervision, J.D.; project administration, Z.L. (Zhangnan Li); funding acquisition, J.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (grant no. 52269010), the Science and Technology Planning Project of Guangxi, China (grant no. AB22035075), and the National Natural Science Foundation of China (grant no. 51979046).

Data Availability Statement: Not applicable.

Acknowledgments: The authors wish to thank the reviewers for their constructive comments.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Ongley, E.D.; Zhang, X.L.; Yu, T. Current status of agricultural and rural non-point source pollution assessment in China. *Environ. Pollut.* **2010**, *158*, 1159–1168. [CrossRef] [PubMed]
- Yi, X.S.; Lin, D.X.; Li, J.H.; Zeng, J.; Wang, D.X.; Yang, F. Ecological treatment technology for agricultural non-point source pollution in remote rural areas of China. *Environ. Sci. Pollut. Res.* 2021, 28, 40075–40087. [CrossRef] [PubMed]
- Xue, L.H.; Hou, P.F.; Zhang, Z.Y.; Shen, M.X.; Liu, F.X.; Yang, L.Z. Application of systematic strategy for agricultural non-point source pollution control in Yangtze River basin, China. *Agric. Ecosyst. Environ.* 2020, 304, 107148. [CrossRef]
- 4. Li, C.H.; Wang, Y.K.; Ye, C.; Wei, W.W.; Zheng, B.H.; Xu, B. A proposed delineation method for lake buffer zones in watersheds dominated by non-point source pollution. *Sci. Total Environ.* **2019**, *660*, 32–39. [CrossRef]
- Wang, H.L.; He, P.; Shen, C.Y.; Wu, Z.N. Effect of irrigation amount and fertilization on agriculture non-point source pollution in the paddy field. *Environ. Sci. Pollut. Res.* 2019, 26, 10363–10373. [CrossRef]
- Zhang, T.; Yang, Y.H.; Ni, J.P.; Xie, D.T. Adoption behavior of cleaner production techniques to control agricultural non-point source pollution: A case study in the Three Gorges Reservoir Area. J. Clean. Prod. 2019, 223, 897–906. [CrossRef]
- He, X.; Shahab, A.; Xi, B.D.; Chang, Q.X.; You, S.H.; Li, J.Y.; Sun, X.J.; Huang, H.W.; Li, X.K. Heavy metal pollution, ecological risk, spatial distribution, and source identification in sediments of the Lijiang River, China. *Environ. Pollut.* 2021, 269, 116189.
- 8. Dai, J.F.; Quan, Q.H.; Fang, R.J.; Zeng, H.H.; Zhang, H.Y.; Xu, Q.X.; Yang, L.C. Estimation of non-point source pollution load in upstream of Lijiang River. *Adv. Sci. Technol. Water Resour.* **2017**, *37*, 57–63. (In Chinese)
- Zhu, D.T.; Cheng, X.J.; Li, W.H.; Niu, F.J.; Wen, J.H. Temporal and Spatial Variation Characteristics of Water Quality in the Middle and Lower Reaches of the Lijiang River, China and Their Responses to Environmental Factors. *Int. J. Environ. Res. Public Health* 2022, 19, 8089. [CrossRef]
- 10. Xiao, Y.T.; Yao, J.; Shen, S.; Fan, M. Temporal and spatial Evolution of Non-point source pollution load of Total Nitrogen in Tuojiang River Basin. *Environ. Sci.* 2021, 42, 3773–3784. (In Chinese)
- Tahmasebi, N.M.; Grimm, K.; Bazrkar, M.H.; Zeng, L.; Shabani, A.; Zhang, X.D.; Chu, X.F. SWAT modeling of non-point source pollution in depression-dominated basins under varying hydroclimatic conditions. *Int. J. Environ. Res. Public Health* 2018, 15, 2492. [CrossRef]
- Wang, Q.R.; Liu, R.M.; Men, C.; Guo, L.J. Application of genetic algorithm to land use optimization for non-point source pollution control based on CLUE-S and SWAT. J. Hydrol. 2018, 560, 86–96. [CrossRef]
- 13. Shen, Z.Y.; Qiu, J.L.; Hong, Q.; Chen, L. Simulation of spatial and temporal distributions of non-point source pollution load in the Three Gorges Reservoir Region. *Sci. Total Environ.* **2014**, *493*, 138–146. [CrossRef]
- 14. Geng, R.Z.; Sharpley, A.N. A novel spatial optimization model for achieve the trad-offs placement of best management practices for agricultural non-point source pollution control at multi-spatial scales. *J. Clean. Prod.* **2019**, 234, 1023–1032. [CrossRef]
- 15. Wang, H.L.; Wu, Z.N.; Hu, C.H.; Du, X.Z. Water and nonpoint source pollution estimation in the watershed with limited data availability based on hydrological simulation and regression model. *Environ. Sci. Pollut. Res.* 2015, 22, 14095–14103.
- 16. Jiang, Y.; Liu, C.M.; Hao, S.N.; Zhao, H.T.; Li, X.Y. A framework to develop a watershed pollution load model for semiarid and semihumid areas. *J. Hydrol.* **2019**, *579*, 124179. [CrossRef]
- 17. Wang, W.Z.; Chen, L.; Shen, Z.Y. Dynamic export coefficient model for evaluating the effects of environmental changes on non-point source pollution. *Sci. Total Environ.* **2020**, 747, 141164. [CrossRef]
- 18. Zhou, G.; Hei, P.F.; Lei, K.; Fu, G.; Qiao, F. Numerical modeling of the relationship between pollution loads and water quality in lower reach of Ganjiang River. *Adv. Water Sci.* **2013**, *24*, 883–893. (In Chinese)
- 19. Yakubu, M.L.; Yusop, Z. Adaptability of rainfall simulators as a research tool on urban sealed surfaces—A review. *Hydrol. Sci. J.* **2017**, *62*, 996–1012. [CrossRef]
- 20. Cheng, X.; Chen, L.D.; Sun, R.H. Modeling the non-point source pollution risks by combing pollutant sources, precipitation, and landscape structure. *Environ. Sci. Pollut. Res.* **2019**, *26*, 11856–11863. [CrossRef]
- 21. Ustaoğlu, F.; Tepe, Y.; Taş, B. Assessment of stream quality and health risk in a subtropical Turkey river system: A combined approach using statistical analysis and water quality index. *Ecol. Indic.* **2020**, *113*, 105815. [CrossRef]

- 22. Chen, Y.Y.; Song, L.H.; Liu, Y.Q.; Yang, L.; Li, D.L. A review of the artificial neural network models for water quality prediction. *Appl. Sci.* 2020, 10, 5776. [CrossRef]
- Kadam, A.K.; Wagh, V.M.; Muley, A.A.; Umrikar, B.N.; Sankhua, R.N. Prediction of water quality index using artificial neural network and multiple linear regression modelling approach in Shivganga River basin, India. *Modeling Earth Syst. Environ.* 2019, 5, 951–962. [CrossRef]
- 24. García-Alba, J.; Bárcena, J.F.; Ugarteburu, C.; García, A. Artificial neural networks as emulators of process-based models to analyse bathing water quality in estuaries. *Water Res.* 2019, 150, 283–295. [CrossRef] [PubMed]
- 25. Ji, H.; Peng, D.; Fan, C.; Zhao, K.; Gu, Y.; Liang, Y. Assessing effects of non-point source pollution emission control schemes on Beijing's sub-center with a water environment model. *Urban Clim.* **2022**, *43*, 101148. [CrossRef]
- 26. Cai, D.S.; Ma, Z.L. Main Ecological Problems in Lijiang River Watershed. J. Guangxi Norm. Univ. (Nat. Sci. Ed.) 2008, 26, 110–112. (In Chinese)
- Li, W.; Huang, H.L.; Yan, J.L.; Li, Y.B. Investigation on Water Pollution of Nanxi River of Guilin City Based on 3S Technology. *Environ. Monit. China* 2012, 28, 141–148. (In Chinese)
- HJ/T 91-2002; Technical Specification for Surface Water and Sewage Monitoring. China Environmental Protection Bureau: Beijing, China; China Environmental Science Press: Beijing, China, 2003. (In Chinese)
- National Environmental Protection Bureau Book Editorial Board. Methods for Monitoring and Analysis of Water and Wastewater, 4th ed.; China Environmental Science Press: Beijing, China, 1989; pp. 210–255. (In Chinese)
- 30. Bulletin of the Second National Pollution Source Survey. Environ. Prot. 2020, 48, 8–10. (In Chinese)
- Zhang, G.H.; Nie, Z.L.; Liu, S.Y.; Chen, Z.Y.; Zhang, C.Y.; Shen, J.M.; Wang, J.Z.; Cheng, X.X.; Zhang, H.S. Characteristic and variation of groundwater recharge resources in the middle reaches of Heihe River basin. *Adv. Water Sci.* 2005, *16*, 673–678. (In Chinese)
- McMahon, T.A.; Peel, M.C. Uncertainty in stage–discharge rating curves: Application to Australian Hydrologic Reference Stations data. *Hydrol. Sci. J.* 2019, 64, 255–275. [CrossRef]
- Yuan, D.Z.; Li, Y.; Chen, L. Research on flow calculation of provincial border cross-sections in un-gauged area. *Yangtze River* 2015, 46, 32–35. (In Chinese)
- 34. Wang, T.H.; Zhang, Z.; Zhang, Z.; Chen, S.W.; Chen, L. Research on the Calculation Method of the Flow of Water Supply Guarantee Rate in Small Southwest Mountainous Area. *China Rural. Water Hydropower* **2014**, *10*, 92–95. (In Chinese)
- Li, X.J.; Liu, S.G.; Liang, M.Y.; Cai, Y.; Gu, S.; Chen, L.M.; Su, S.H.; Jiang, L.X.; Chen, L.G.; Wu, Q.F.; et al. Innovation and Application of Key Technology for Water Quality and Water Safety of Lijiang River. In Proceedings of the Guangxi Science and Technology Progress Award, Nanning, China, 4 April 2018. (In Chinese).
- Dai, J.F.; Han, P.L.; Zheng, Y.L.; Fang, R.J. Analysis and Characteristics of Inflow Runoff Components in Reservoir Catchment. J. Guilin Univ. Technol. 2013, 33, 438–442. (In Chinese)
- 37. Xu, J.X.; Dai, J.F. Trend Test on Water Quality in the Upper Reaches of Lijiang River in Recent Years. *Pearl River* 2018, 39, 6–10. (In Chinese)
- Zhou, Y.L. Real-time probabilistic forecasting of river water quality under data missing situation: Deep learning plus postprocessing techniques. J. Hydrol. 2020, 589, 125164. [CrossRef]
- Lin, F.; Chen, X.W.; Yao, H.X. Evaluating the use of Nash-Sutcliffe efficiency coefficient in goodness-of-fit measures for daily runoff simulation with SWAT. J. Hydrol. Eng. 2017, 22, 05017023. [CrossRef]
- Moriasi, D.N.; Arnold, J.G.; Van Liew, M.W.; Bingner, R.L.; Harmel, R.D.; Veith, T.L. Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. *Trans. ASABE* 2007, *50*, 885–900. [CrossRef]
- 41. Donigian, A.S.; Imhoff, J.C.; Bicknell, B.R. Predicting water quality resulting from agricultural nonpoint source pollution via simulation-HSPF. In *Agricultural Management and Water Quality*; Iowa State University Press: Ames, IA, USA, 1983.
- 42. Ramanarayanan, T.S.; Williams, J.R.; Dugas, W.A.; Hauck, L.M.; McFarland, A.M.S. Using APEX to Identify Alternative Practices for Animal Waste Management; ASAE: Washington, DC, USA, 1997.
- Motovilov, Y.G.; Gottschalk, L.; England, K.; Rodhe, A. Validation of distributed hydrological model against spatial observations. Agric. For. Meteorol. 1999, 98, 257–277. [CrossRef]
- 44. Santhi, C.; Arnold, J.G.; Williams, J.R.; Dugas, W.A.; Srinivasan, R.; Hauck, L.M. Validation of the SWAT model on a large river basin with point and nonpoint sources. *J. Am. Water Resour. Assoc.* **2001**, *37*, 1169–1188. [CrossRef]
- 45. Singh, J.; Knapp, H.V.; Arnold, J.G.; Demissie, M. Hydrological modeling of the Iroquois river watershed using HSPF and SWAT¹. *JAWRA J. Am. Water Resour. Assoc.* **2005**, *41*, 343–360. [CrossRef]
- 46. Singh, S.K.; Pahlow, M.; Booker, D.J.; Shankar, U.; Chamorro, A. Towards baseflow index characterisation at national scale in New Zealand. *J. Hydrol.* **2019**, *568*, 646–657. [CrossRef]
- 47. Zhu, Y.; Chen, L.; Wang, K.; Wang, W.; Wang, C.; Shen, Z. Evaluating the spatial scaling effect of baseflow and baseflow nonpoint source pollution in a nested watershed. *J. Hydrol.* **2019**, *579*, 124221. [CrossRef]
- 48. Zhang, H.; Li, H.F.; Yu, H.R.; Chen, S.Q. Water quality assessment and pollution source apportionment using multi-statistic and APCS-MLR modeling techniques in Min River Basin, China. *Environ. Sci. Pollut. Res.* **2020**, *27*, 41987–42000. [CrossRef] [PubMed]
- 49. Zhang, X.Q.; Chen, P.; Dai, S.N.; Han, Y.H. Analysis of non-point source nitrogen pollution in watersheds based on SWAT model. *Ecol. Indic.* 2022, 138, 108881. [CrossRef]