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The Spatiotemporal Variations and Potential Causes of Water Quality of Headwaters of Dongjiang River, Southeastern China

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Abstract: Due to the steep slope and short concentration time of flow in mountainous areas, the water environment of headwaters is easily disturbed by human activities. The spatial-temporal variation of the water environment is a key issue for the implementation of river restoration. This study aims to explore the spatial-temporal characteristics of water quality and its pollution sources of the headwaters of the Dongjiang River. Water quality monitoring data over the past 6 years were collected and analyzed using principal component analysis, equal standard pollution load, and multivariate statistical analysis. The results show that the water quality presents significant spatial heterogeneity, where the water quality in the middle and lower reaches is poor. The concentrations of ammonia nitrogen and total phosphorus in the middle and lower reaches were 18.3 and 9.5 times higher than those in the upper reaches, respectively. The water quality has tended to improve recently because of ecological compensation and environmental management. Correlation analysis shows that there were significant positive relationships among major pollutants. Critical source areas were identified, which implies that the most polluted area is located in the middle reaches. Studies have also shown that the water pollution mainly comes from livestock and poultry breeding, industrial sewage discharge, and cultivated land. Controlling the scale of construction land and adjusting the industrial structure is one of the main measures for eradicating water environment problems in headwaters in mountainous areas.

Keywords: ammonia nitrogen; Dongjiang River; spatiotemporal variations; land use

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1. Introduction

With the increase of population and rapid socio-economic development of China, the water quality of river basins is increasingly disturbed by human activities, which has attracted the attention of scientists, the public, and policy makers [1–4]. Researchers have carried out a lot of work on the sources of pollution loads, the spatial and temporal differences of the water quality, and the influence factors of the water environment of river basins [5–8]. Previous studies show that both point source pollution and non-point source pollution have important impacts on the water environment of the river basins [9–12]. Moreover, discharge pollutants from industrial activities also results in the increased pollution of freshwaters, which may hamper human health in nearby areas [12,13].

Most of those studies mainly focus on large rivers or watersheds, while relatively few studies have reported on the water environment of headwaters or small mountain watersheds. Actually, the water environment in the headwaters has fundamental impacts on the water quality in the middle and lower reaches of the river basins [14,15]. Because the headwaters are usually located in high mountains or hills, the hydrological characteristics are significantly different from those of the middle and lower reaches of the plain or estuary area, which in turn leads to a small water environment capacity in the headwaters area and is easily affected by human activities [16].

The Dongjiang River is an important source of drinking water for Hong Kong, and its water quality directly affects the drinking water safety and sustainable economic development of more than 7 million people. The Xiali River is a secondary tributary of the Dongjiang River. Its drainage area accounts for 5.76% of the source area of the Dongjiang River and its flow accounts for 0.56%. The economic proportion of livestock and poultry breeding industries is large, and the population is concentrated. In the past 20 years, with rapid social and economic development, the pollution problem of the watershed has become increasingly prominent, resulting in the industrial water area being rated as inferior V all year around according to the state standard of surface water environment quality of China (GB3838-2002) [17].

In recent years, scholars have carried out extensive research on the water environment pollution in the Dongjiang River basin. For example, Zhang et al. [18] estimated the discharge of commonly used antibiotics in the Dongjiang River basin based on the usage, excretion, wastewater treatment rate, population, and animal numbers of 36 commonly used antibiotics. Hu et al. [19] discussed the occurrence, epigenetic toxicity characteristics, and main toxic pollutants of persistent organic pollutants in surface water of the Dongjiang River basin. These research results provide a scientific basis for the research on water resources' carrying capacity and drinking water safety in the basin, and most of them focus on large-scale research on water-polluted aquatic organisms in the Dongjiang River basin. However, to the best of our knowledge, the water environment status in the headwaters of the Dongjiang River and its relationship with human activities have not yet been studied. Considering that the source region of the Dongjiang River is facing the dual pressures of economic development and water resource protection, it is necessary to conduct research on the temporal and spatial changes of the water environment in this region.

The objectives of this study were to (1) analyze the temporal and spatial characterization of the water quality in the headwaters of the Dongjiang River, (2) identify the main sources of water pollution loads in the headwaters of the Dongjiang River, and (3) reveal the relationship between the water environment and land use in the headwaters of the Dongjiang River. The emission of pollutant loads from different pollution sources and their temporal and spatial characteristics are crucial for the refined management and control of the long-term sustainable water supply guarantee system in the Guangdong-Hong Kong-Macao Greater Bay Area.

2. Materials and Methods

2.1. Study Area

The Xiali River originates from Dashijing Mountain, Lishi Town, Dingnan County, and flows from northwest to southeast through Lishi Town and Tianjiu Town, which make up the main urban area of Dingnan County. Liheng Reservoir is located on the upstream of the Xiali River and has a catchment area of 37.5 km^2 and a storage capacity of 38.6 million m^3 (see Figure 1). Based on environmental management of water resources of local government, the Xiali River is divided into three water functional areas: drinking water source area, industrial water area, and reserve area, with the target water quality of Class II-III, Class IV, and Class III, respectively, according to the state standard of surface water environment quality of China (GB3838-2002) (Figure 1). The upper limits of ammonia nitrogen were 0.15 mg/L, 0.5 mg/L, 1.0 mg/L, 1.5 mg/L, and 2.0 mg/L for Class I, II, III, IV, and V water, respectively, and the upper limits of total phosphorus were 0.02 mg/L, 0.1 mg/L, 0.2 mg/L, 0.3 mg/L, and 0.4 mg/L for Class I, II, III, IV, and V water, respectively. The basin has a total population of about 113,500.

The Xiali River has a typical subtropical humid monsoon climate in hilly areas, with rich heat, abundant rainfall, and four distinct seasons. The average annual temperature is

18.9 °C, with the highest temperature being 41 °C and the lowest temperature being −8 °C. The dominant wind direction is north-northwest wind. The average relative humidity is 80% and the average dryness index is 0.54. There is no freezing phenomenon in winter rivers, and the frost-free period is 293 days, accounting for 80% of the annual days. The average annual rainfall was 1587.0 mm, with 31.9% occurring from April to June, and 22.1% occurring from November to March of the following year. The maximum annual rainfall (2016) was 2491 mm, and the minimum annual rainfall (1963) was 916.4 mm. The annual variability is 2.33 times, and the average number of rainfall days is about 161 days.

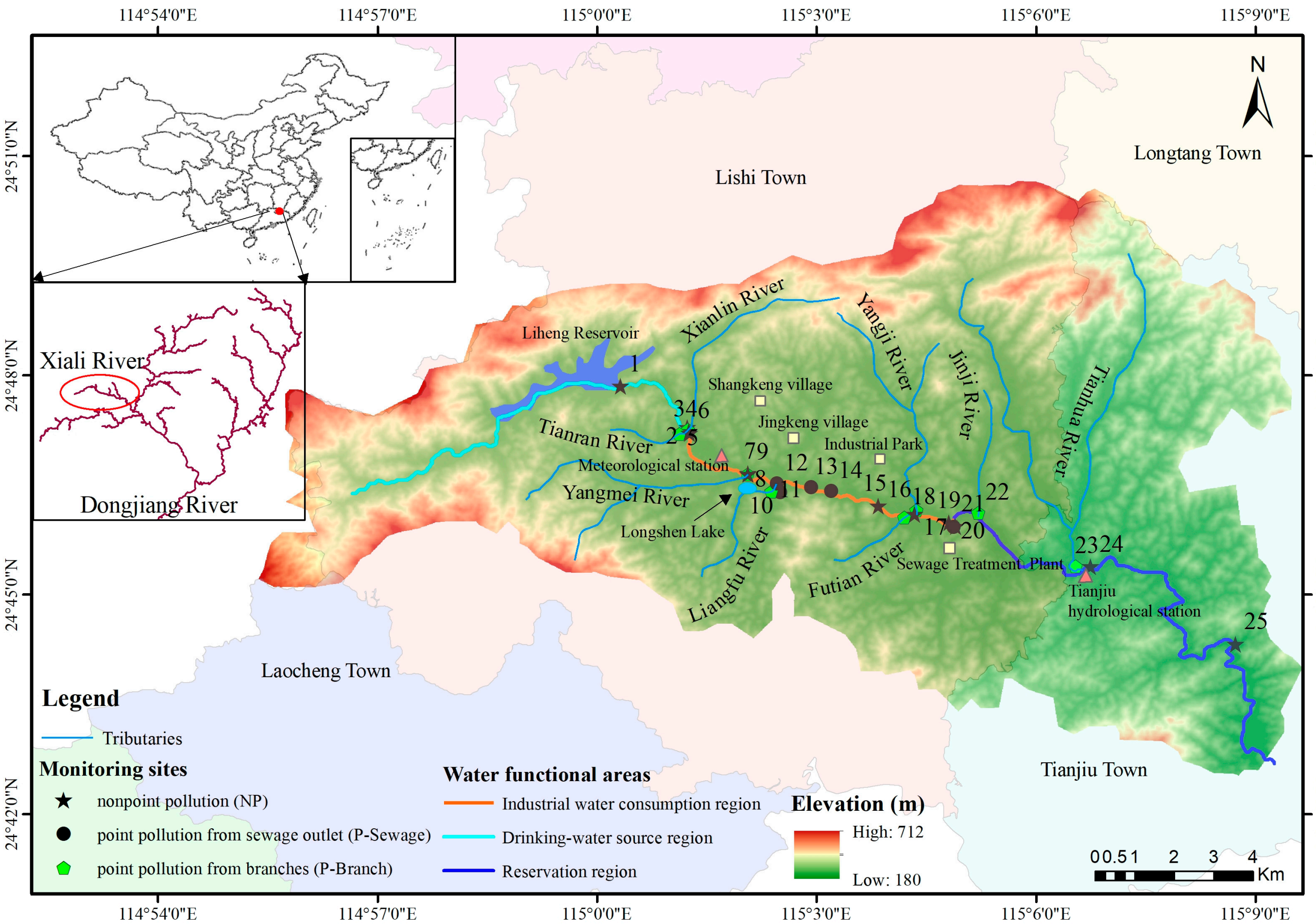

Figure 1. The monitoring sites of the study area.

The cultivated land area in the basin is about 40 km^2, accounting for 20% of the total area, mainly planting navel oranges, camellia, and rice. The scale of pig breeding in the basin is large. Dingnan County is among the top ten pig breeding counties of China, with the annual slaughter of more than 500,000 pigs. The Xiali River is one of the main areas of pig farming. As the Xiali River passes through the main urban area and industrial park of Dingnan County, the population and number of industrial enterprises in the basin is high. Agricultural non-point source pollution and industrial and urban sewage point source pollution have serious and complex effects on the water quality of the Xiali River.

2.2. Data Collection and Preparation

Water quality data were obtained from Hydrology and Water Resources Monitoring Center in the upper Ganjiang River. Twenty-five monitoring sections were investigated along the 20 km reach of the river (Figure 1) considering tributaries and point pollutions. Water sampling on three representative sections, i.e., upstream #1, midstream #21, and downstream #24, were conducted monthly from January 2015 to November 2020, with

216 observations in total. To illustrate the critical source area of water pollution, water sampling on 25 major sections was conducted synchronously in 2020. Eight parameters were used as representative indicators in this paper, i.e., water temperature (WT), pH, dissolved oxygen (DO), permanganate index (COD_{mn}), biochemical oxygen demand (BOD_5), ammonia nitrogen (NH_3-N), total phosphorus (TP), and fluoride (F). The toxic heavy metals (e.g., Hg, Pb, As, Cd, Cr) were not explored in this study because of the low concentrations of toxic metal parameters compared to the state standard of surface water environment quality of China (GB3838-2002) for heavy metals.

This paper uses the method recommended by the state standard of surface water environment quality (GB3838-2002) to detect water quality. Some indicators of water quality were measured in situ, using a YSI ProPlus Multiparameter Instrument in the field, including the water temperature, pH, and dissolved oxygen. To ensure the effectiveness of water quality detection, water samples were kept in plastic buckets and transferred to the laboratory with a cooler filled ice. The BOD_5 is an important parameter indicating the degree of water pollution caused by organic matter and measured as the variation in the oxygen concentration using dilution and seeding methods [20]. The concentrations of COD_{mn} were assayed by titrimetric analysis under potassium permanganate oxidation [20]. The concentrations of TP were measured using ammonium molybdate spectrophotometry method. The contents of NH_3-N were analyzed spectrophotometrically using the nesslerization method [20]. The contents of F were measured using an ion chromatography system [20].

2.3. Methods

In general, three statistical methods were used in this study, including time series analysis and correlation analysis, principal component analysis and stepwise regression analysis. In addition, the equal standard pollution load method was used to identify the key pollution source areas. Time series analysis was used to explore changes in water quality indicators over time, including interannual and seasonal variations. The article uses bivariate Pearson correlation in SPSS 24.0 to explore the relationship between water quality indicators. To illustrate the possible influences of land use on water quality, stepwise regression analysis was applied to quantify the relationship between them using stepwise function in MATLAB (version, 2016b).

The principal component analysis (PCA) is a mathematical method commonly used in environmental research to minimize the redundant information of raw data. PCA eliminates overlapping information using projection methods and the principle of it ensures the minimum loss of original information. It is widely applied to study the underlying relationships among variables. The original data were processed using SPSS 24.0. The KMO (Kaiser–Meyer–Olkin) test and Bartlett's test of sphericity were used to check the data normality for further analysis, where the closer the KMO index is to 1, the more suitable for PCA [20–22]. The results show that the KMO index was 0.734, and the significance level of Bartlett's test of sphericity was smaller than 0.001, indicating the useful analysis of datasets for PCA.

The equal standard pollution load method was adopted to identify the critical source areas of pollution [23,24]. The equal standard pollution load method is calculated using the ratio of the pollutant discharge and the target water quality of specific pollutant. In this paper, the equal standard pollution load of ammonia nitrogen and total phosphorus were analyzed based on the threshold concentration of pollutants according to the target water quality in GB3838-2002. The result of the equal standard pollution load indicates the amount of water required if the pollutants are diluted to the discharge standard.

3. Results

3.1. The Change of Water Quality over Time and Reaches

Figure 2 plots the temporal change of water quality parameter concentrations in different reaches of the Xiali River. The water temperature presents a significant pattern with high in summer and low in winter, which are affected by the seasonal changes of air temperature. The difference in water temperature between the upper, middle, and lower reaches is small. The pH of the upper reaches is higher than that of the middle and lower reaches, reflecting that the upstream rivers are more alkaline (about 7.6), and the middle and lower reaches are more acidic (about 6.9). From 2015 to 2020, the dissolved oxygen in the Xiali River showed a slight decreasing trend, and the dissolved oxygen in the upper reaches was slightly higher than that in the middle and lower reaches. The inter-annual and intra-annual changes of permanganate index and 5-day biochemical oxygen demand were obvious, and there was no significant change trend.

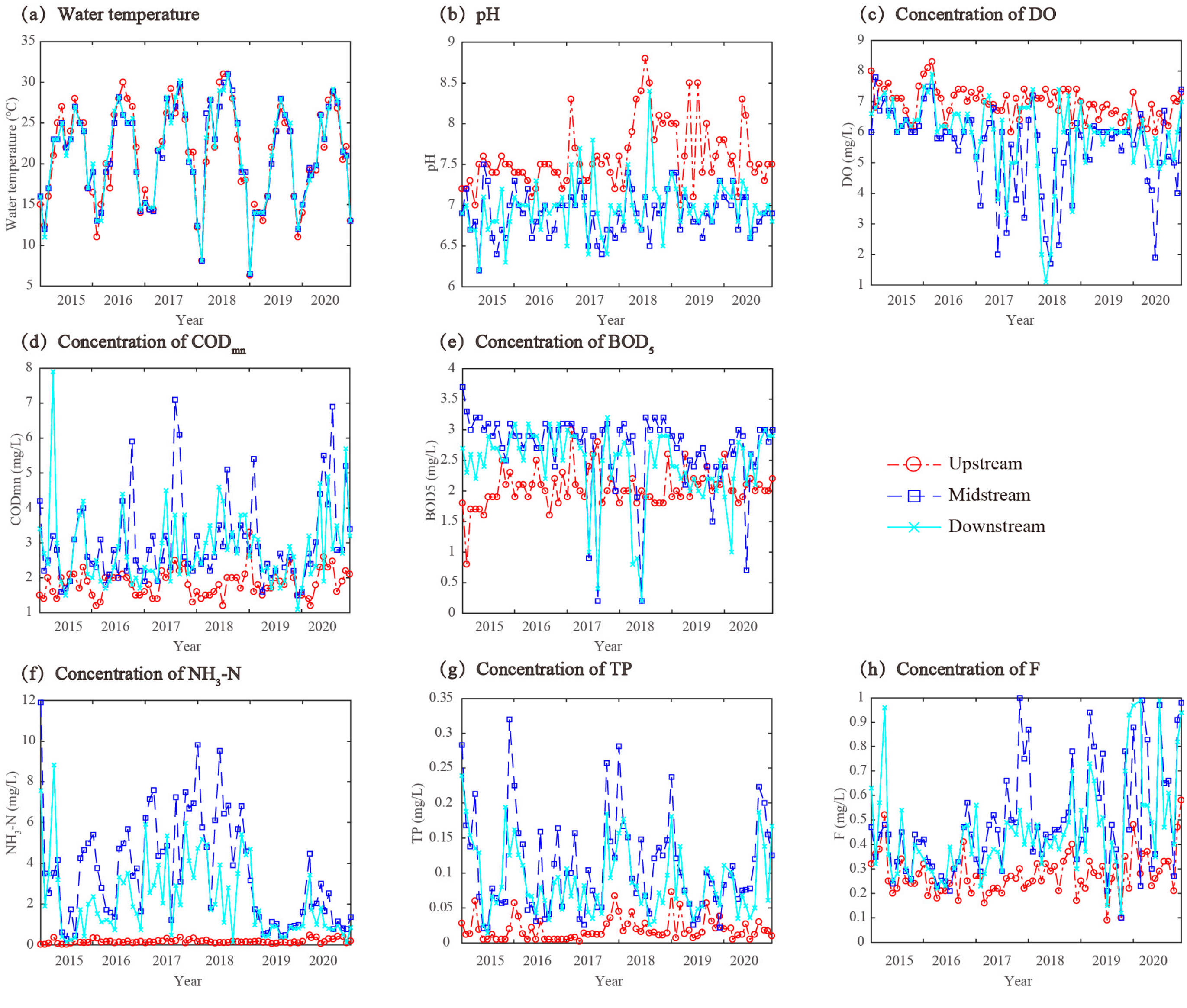

Figure 2. Concentration of water quality of the Xiali River during the period from 2015–2020.

The concentrations of ammonia nitrogen, total phosphorus, and fluoride in the upper reaches of the Xiali River were significantly lower than those in the middle and lower reaches, and the concentrations of ammonia nitrogen, total phosphorus, and fluoride in the middle and lower reaches were 18.3, 9.5, and 1.7 times higher than those in the upper reaches, respectively. The pollution of nitrogen, phosphorus, and fluoride in middle and lower reaches is more serious than upstream. From 2015 to 2017, the ammonia nitrogen pollution in the middle and lower reaches showed an increasing trend. In 2017, the ammonia nitrogen concentration was up to 7.58 mg/L. From 2018 to 2019, the ammonia nitrogen concentration in the middle and lower reaches dropped sharply, and it rebounded significantly in 2020. From 2015 to 2020, the total phosphorus in the middle and lower reaches of the Xiali River showed a downward trend in fluctuations. The maximum concentration of total phosphorus in 2020 was 0.097 mg/L lower than that in 2015. The concentration of fluoride in the middle and lower reaches of the Xiali River has a weak growth trend during the period from 2015–2020, and the average concentration of fluoride in 2020 is 1.6 times that of 2015.

Figure 3 shows that the concentration of pollutants presents a certain seasonal difference. On the whole, the concentration of pollutants in the dry season in winter is high, and the concentration of pollutants in the wet season (spring and summer) is low. In order to explore the statistical significance of the seasonal differences of each water quality parameter, the box plots of each water quality parameter concentration in the wet season and dry season, and the differences between them, are drawn in Figure 3. Based on the analysis of the flow of the Xiali River, the lowest flow appears in December, January, and February, and the peak flow frequently appears in June, so the paper takes May to July as the wet season, and December, January, and February as the dry season. Figure 3 shows that the seasonal differences of water temperature and total phosphorus are the most significant. Except for total phosphorus in the upstream, the significance of such differences reaches 0.01. The seasonal difference of dissolved oxygen and ammonia nitrogen was 0.1 in the upstream and middle reaches, 0.05 in the downstream, and 0.01 in the downstream. Other water quality parameters show different seasonal differences in different river reaches. For some indicators, the seasonal differences are significant in the downstream but insignificant in the upstream, such as fluoride; for other indicators, the seasonal differences are significant in the upstream but insignificant in the downstream, such as permanganate index.

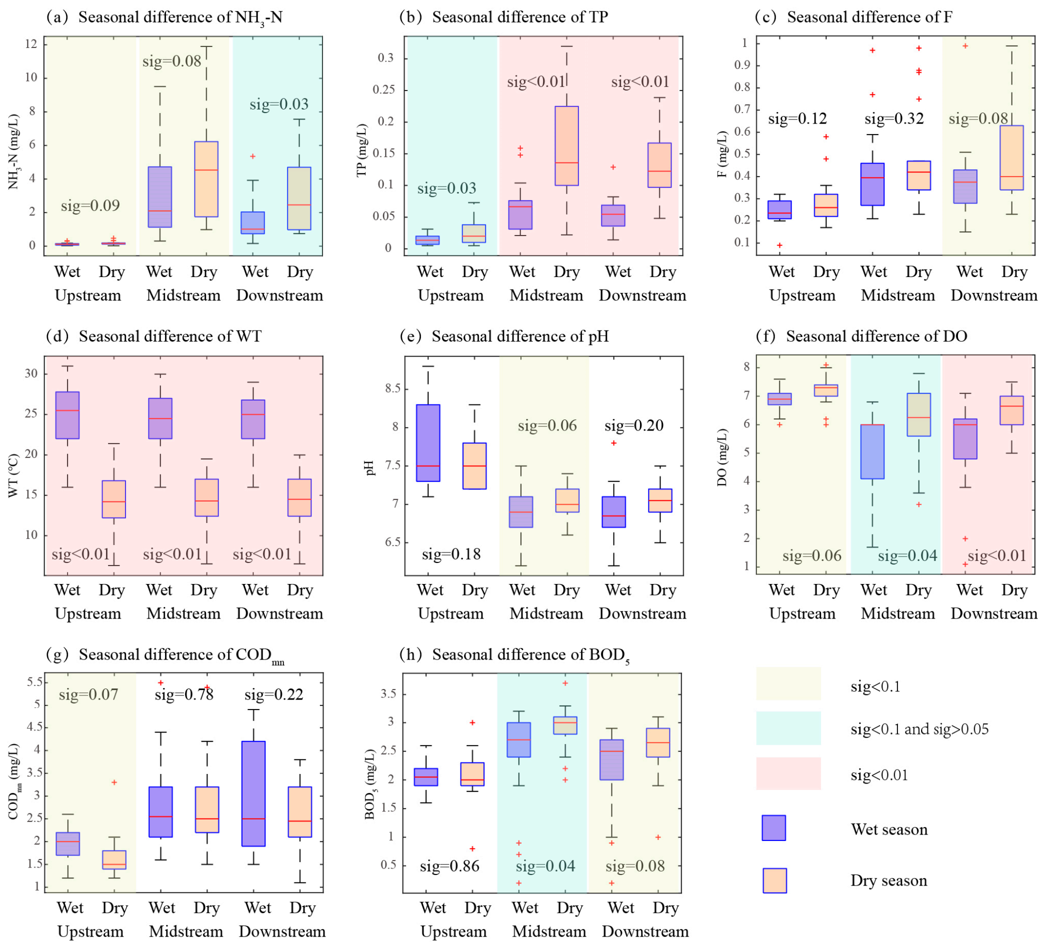

Figure 3. Seasonal difference of concentration of water quality of the Xiali River.

3.2. The Correlation and PCA of Water Quality

The correlations of water quality parameters of the Xiali River are shown in Figure 4. In general, there were significant correlations among most water quality parameters, including positive and negative correlations. There was a significant negative correlation between WT, pH, DO and COD_{mn}, BOD_5, NH_3-N, TP, and F, among which the correlation between pH and COD_{mn}, NH_3-N, and TP was more than 0.4, the correlation between DO and COD_{mn} was 0.45, and the correlation between DO and NH_3-N was 0.39. At the same time, there were significant positive correlations among organic pollutants (COD_{mn}, BOD_5), nitrogen and phosphorus pollutants (TP, NH_3-N), and fluoride (F). For example, the correlations between COD_{mn} and NH_3-N, TP, and F were 0.45, 0.34, and 0.37, respectively. It is worth noting that there is a significant positive correlation between NH_3-N and TP, with a correlation of 0.63. However, TP has a significant negative correlation with WT, while NH_3-N has no significant negative correlation with WT.

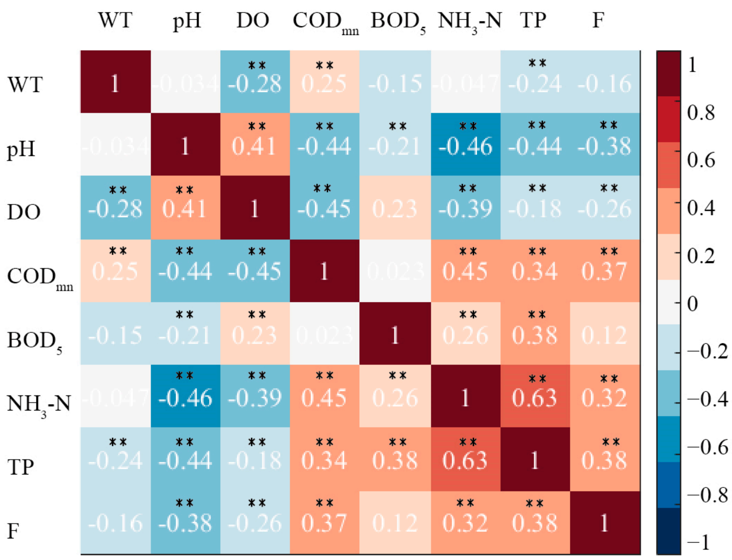

Figure 4. Heatmap of water quality parameters, ** represents 99% significance.

After standardized processing of the original data, the KMO test and Bartlett sphericity test were used for the applicability test, and the following eight indicators were screened out: the KMO value of WT (X1), pH (X2), DO (X3), COD_{mn} (X4), BOD_5 (X5), NH_3-N (X6), TP (X7), and F (X8) was 0.73, that is, there was a certain correlation between indicators, and the SIG value of Bartlett's sphericity test was less than 0.05. It shows that each index is not independent of the others and meets the requirements of principal component analysis. The results of the principal component analysis are shown in Table 1. The results showed that the first three principal components accounted for a total of 70% of the results (Table 1), which was close to 75.0%. It can be considered that the results of this principal component analysis were relatively reliable.

Table 1. The component matrix of the water quality indicators.

Component	Initial Eigen Values			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.038	37.974	37.974	2.837	35.463	35.463
2	1.658	20.723	58.698	1.484	18.554	54.017
3	0.918	11.479	70.176	1.293	16.160	70.176
4	0.692	8.652	78.828			
5	0.563	7.039	85.867			
6	0.460	5.749	91.616			
7	0.360	4.500	96.116			
8	0.311	3.884	100			

According to the results of principal component analysis, the first, second, and third principal components were extracted to draw the principal component load map of water quality parameters (Figure 5). The results show that DO and pH in the first principal component are the negative load with values lager than 0.6. Ammonia nitrogen, total phosphorus, fluoride, and permanganate index in the first principal component are positive load with values 0.5~0.8, while they are lower load in the second and third principal component. BOD_5 is the main factor of the second principal component, with a load of 0.9, which is small in the first and third principal components. Water temperature is the main influencing factor of the third principal component, and the load reaches −0.88, which is smaller in the first and second principal components.

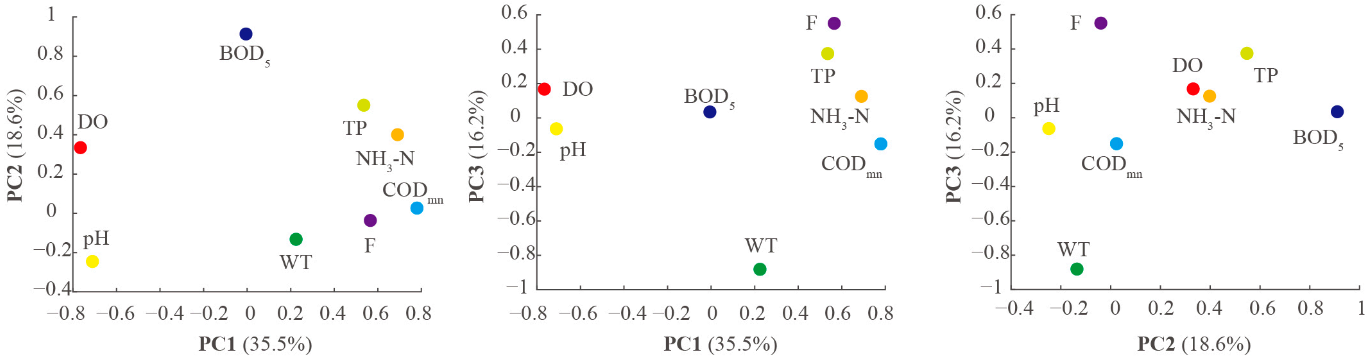

Figure 5. Principal component analysis load diagram of water quality parameters.

3.3. The Critical Source Areas of Water Quality

Table 2 shows the results of the equal standard pollution load using the data of ammonia nitrogen, total phosphorus, chemical oxygen demand, and discharge of 25 major sections synchronously monitored in the summer of 2020. The monitored sections were classified in three types: eight tributaries as branch point sources, six sewage outlets as common point sources, and the rest as mainstream non-point sources. It can be seen that the pollution contribution of the eight tributaries from large to small are Liangfu River, Yangmei River, Xiaozhong River, Xianling River, Yangji River, Tianran River, Futian River, and Jinji River. The standard load ratios of pollution sources are 4.94%, 2.66%, 0.65%, 0.39%, 0.12%, 0.03%, 0.02%, and 0.01%, respectively. The equal standard pollution load ratio of all tributary pollution sources is 8.82%.

The point source pollution load of sewage outlets is 21.3%, and the largest is Longshen Lake and Dingnan Industrial Park, which are 13.7% and 2.5%, respectively. The pollution load of 11 sections of the mainstream was 69.8%, and the top three were the Xiali River Sewage Treatment Plant, Dingnan Substation, and Dingnan Tianjiu, accounting for 16.7%, 15.3%, and 13.3%, respectively. The pollution ratio of branch point source, common point source, and mainstream non-point source is 1:3:8.

The standard pollution load ratio of pollutants between ammonia nitrogen, total phosphorus, and chemical oxygen demand are 72.9%, 13.8%, and 13.8%, respectively. Compared with the surface water environmental quality standard of China (GB3838-2002), ammonia nitrogen exceeded the target water concentration except for the section of the Liheng Reservoir, total phosphorus exceeded the target concentration by three points, and chemical oxygen demand was within the target water concentration range. Therefore, the priority control pollutant in the Xiali River basin is ammonia nitrogen. The non-point source pollution in the mainstream is dominant, including urban domestic sewage and large-scale livestock and poultry breeding pollution, etc. The most polluted area are the rivers between the Yangmei River and Dingnan substation, which should demand priority attention.

Table 2. Equal standard pollution load of main pollutants and pollution sources.

Monitoring Sites	Discharge ($m^3 \cdot s^{-1}$)	Concentration ($mg \cdot L^{-1}$)			Equal Standard Pollution Load ($t \cdot a^{-1}$)			Percentage of Pollution Load among River Basin (Kn) (%)	Order of Pollution Load	Pollution Types **
		NH_3-N	TP	COD	NH_3-N	TP	COD			
1	0.001	0.18	0.01	7.7	0.01	0.00	0.01	0.00	25	NP
2	0.005	2.62	0.108	7.2	0.28	0.06	0.04	0.04	20	NP
3	0.016	5.96	0.266	8.2	3.01	0.45	0.14	0.39	15	P-Branch
4	0.017	5.16	0.23	7.96	1.85	0.41	0.14	0.26	17	NP
5	0.001	6.11	0.327	9.3	0.19	0.03	0.01	0.03	22	P-Branch
6	0.018	6.08	0.32	12.2	2.30	0.61	0.23	0.34	16	NP
7	0.061	4.52	0.176	4.6	5.80	1.13	0.29	0.79	12	NP
8	0.075	7.78	0.544	22.1	18.40	4.29	1.74	2.66	9	P-Branch
9	0.136	4.65	0.199	3.4	13.30	2.84	0.49	1.81	11	NP
10	0.12	18.1	1.113	343	68.50	14.04	43.27	13.71	3	P-Sewage
11	0.12	13.8	0.728	10.2	34.82	9.18	1.29	4.94	7	P-Branch
12	0.015	90.9	0.284	1246	2.87	0.45	19.65	2.50	10	P-Sewage
13	0.004	6.86	0.431	14.4	0.06	0.18	0.06	0.03	21	P-Sewage
14	0.001	5.06	1.334	1292	0.01	0.14	1.36	0.16	18	P-Sewage
15	0.047	1.96	3.267	485	0.58	16.14	23.96	4.43	8	P-Sewage
16	0.095	0.11	0.049	3.2	0.35	0.49	0.32	0.13	19	P-Branch
17	0.436	7.17	0.324	16.2	65.72	14.85	7.42	9.59	6	NP
18	0.006	0.67	0.08	6.7	0.13	0.05	0.04	0.02	23	P-Branch
19	0.440	12.9	0.573	16.4	119.33	26.50	1.57	16.72	1	NP
20	0.116	3.25	0.161	3.2	2.38	1.96	0.39	0.52	14	P-Sewage
21	0.550	10.5	0.173	15.0	121.41	10.00	8.67	15.27	2	NP
22	0.0027	0.45	0.031	3.3	0.04	0.01	0.01	0.01	24	P-Branch
23	0.219	0.24	0.092	3.2	1.69	3.18	1.11	0.65	13	P-Branch
24	0.434	7.21	0.198	14.3	98.68	13.55	9.79	13.30	4	NP
25	0.521	5.74	0.125	3.4	94.31	10.27	2.79	11.70	5	NP

** NP: nonpoint pollution, P-Branch: point pollution from branches, P-Sewage: point pollution from sewage outlet.

4. Discussion

4.1. Spatial Difference of Water Quality and the Influence of Land Use in Headwaters

The results showed that the water quality of the Xiali River showed significant spatial differences. Organic matter pollution (represented by COD_{mn} and BOD_5) usually comes from the discharge of domestic sewage or industrial wastewater, the decomposition of animals and plants into the water body, etc. [25–27]. COD_{mn} and BOD_5 in the middle and lower reaches of the Xiali River were 2.38 times higher than those in the upper reaches, indicating that organic matter pollution was serious in the middle and lower reaches. The middle reaches of the Xiali River flow through the main urban area of Dingnan County, with a population of 130,000. The urban domestic sewage discharge is about 2.73 million tons per year. At the same time, the chemical industry and circuit board manufacturing enterprises in Dingnan Industrial Park discharge industrial wastewater, which is one of the main reasons for the most serious organic matter pollution in the middle reaches. The lower reaches of the Xiali River have large, cultivated areas, mainly for the purposes of planting rice, navel oranges, and oil tea. Agricultural non-point source pollution may lead to serious organic matter pollution in the lower reaches [12,28,29].

The spatial difference of nitrogen and phosphorus pollutants is similar to organic pollution. The pollution degree of the middle and lower reaches of the Xiali River is more severe than that of the upstream, and the spatial difference of nitrogen and phosphorus is more significant than that of organic pollution. NH_3-N and TP are mainly derived from agricultural non-point source pollution [30–32]. The agricultural industry is dominated by pigs, navel oranges, and oil tea in Li Town and Tianjiu Town of Dingnan County, which are developing rapidly, and there are several demonstration bases for cultivation, such as bamboo shoots on one thousand acres in Zhongzhen village, navel oranges on ten thousand acres in Jingkeng village, pig breeding of more than 10,000 pigs per year in Shangkeng village, and high-quality tea seedlings of 15 million in Chebu village. The emissions of livestock and poultry are one of the important reasons for the serious nitrogen and phosphorus pollution in the downstream of the river.

Many studies have shown that land use exerts great influence on the water environment of the basin. Construction land generally has a positive correlation with nitrogen and phosphorus, while forest land generally has a negative correlation with nitrogen and phosphorus concentration in water. For example, the latest research found that construction land has a typical positive correlation with ammonia nitrogen concentration, total phosphorus concentration, and COD_{mn} [33]. According to Wang et al. [34], urban land is the main source of TP, NH_3-N, and COD_{mn} in the Ganjiang River basin during the wet season. A study on the Liuxi River found that residential land, transportation land, cultivated land, and water quality indicators were significantly positively correlated, while forest land was significantly negatively correlated with water quality indicators [35]. The research in the middle region of the Yellow River also demonstrated the positive impact of vegetation on surface water quality [36].

Stepwise regression analysis further quantitatively revealed the relationship between land use type and N and P pollution and COD_{mn}. Sub-catchments of all monitoring sites were extracted except those sites of point pollution from sewage outlets, i.e., #12, #13, #14, #15, #19, and #20. Land use of those sub-catchments and corresponding water quality parameters were analyzed using stepwise function in MATLAB (version, 2016b). Equations (1)–(3) show that nitrogen and phosphorus concentration in the Xiali River is significantly positively correlated with the proportion of construction land, COD_{mn} is negatively correlated with the proportion of grassland area, and positively correlated with the proportion of shrub land area. The coefficient of the regression equation between ammonia concentration and the proportion of construction land was 0.28, and the coefficient of the regression equation between total phosphorus concentration and the proportion of construction land was 0.016, indicating that ammonia nitrogen concentration was more sensitive to the proportion of construction land than total phosphorus concentration. The expansion of construction land may lead to the further increase of ammonia nitrogen concentration in the Xiali River (Figure 6). Meanwhile, the intercept of the regression equation between ammonia nitrogen concentration and the proportion of construction land was 1.70, while the intercept of the regression equation between total phosphorus concentration and construction land was 0.024, which reflected that the ammonia nitrogen concentration was affected by both the proportion of construction land and other factors, and the ammonia nitrogen concentration seriously exceeded the water quality target of the water environment functional area.

$$\mathrm{NH_3N} = 0.28\mathrm{AS} + 1.70, \mathrm{R}^2 = 0.54, p < 0.001 \quad (1)$$

$$\mathrm{TP} = 0.016\mathrm{AS} + 0.024, \mathrm{R}^2 = 0.56, p < 0.001 \quad (2)$$

$$\mathrm{CODmn} = -1.54\mathrm{GL} + 5.83\mathrm{SL} + 25.9, \mathrm{R}^2 = 0.45, p = 0.007 \quad (3)$$

where AS represents the proportion of built-up land area (%), GL represents the proportion of grassland area (%), and SL represents the proportion of shrub land area (%).

4.2. Temporal Change of Water Environment and Ecological Environment Management

Due to the unique characteristics of natural geography of small watersheds in mountainous areas, e.g., the catchment area is small, the slope is large, and the concentration time of flow is short, the change of water environment is more sensitive to the development of social economy and ecological environmental management [16]. As an important tributary of the Dongjiang River, the Xiali River has a poor water environment quality, in particular, severe ammonia nitrogen pollution, which is a key area for water environment control in the headwaters of the Dongjiang River. It is found that ammonia nitrogen pollution in the middle and lower reaches of the Xiali River is an important cause of local water environmental problems. Ammonia nitrogen concentration in the Xiali River showed a significant downward trend during the period from 2015–2020 and decreased by 70% from 2018 to 2019. The ammonia nitrogen load of the Xiali River mainly comes from urban sewage discharge, industrial wastewater discharge, and livestock and poultry breeding sewage discharge.

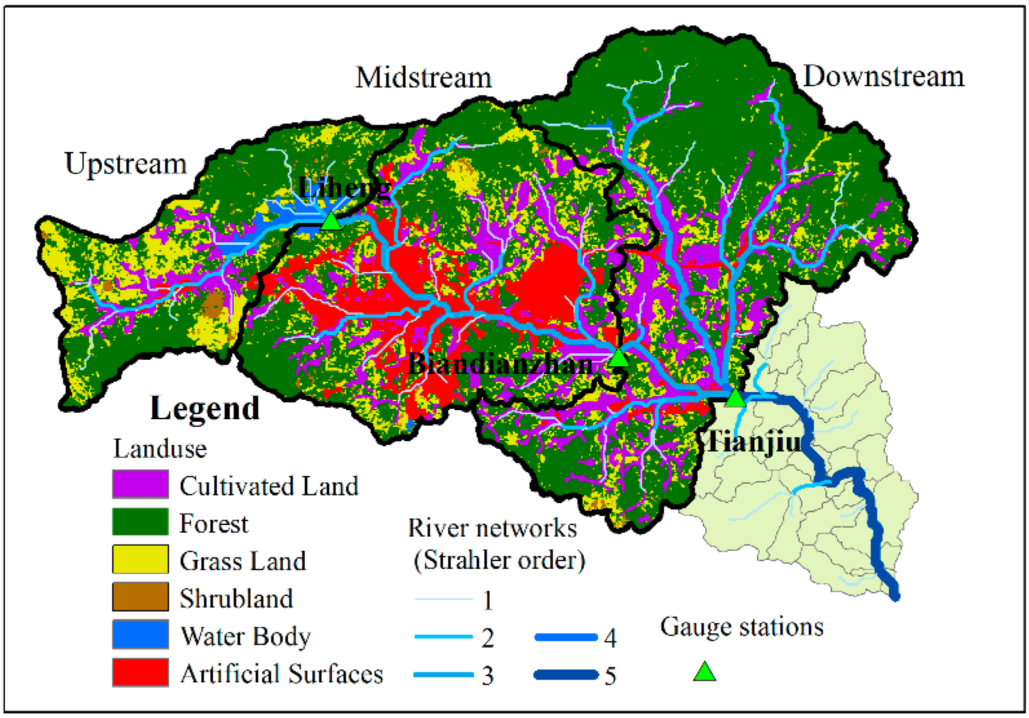

Figure 6. Land use types in the Xiali River basin (2020).

With the development of horizontal ecological compensation and ecological environmental management projects in the upper and lower reaches of the Dongjiang River basin, ammonia nitrogen emissions in the Xiali River basin has been controlled to a certain extent. For example, Dingnan County Futian Industrial Park sewage treatment plant was built in 2014, where the daily treatment scale reaches 10,000 cubic meters. Dingnan County domestic sewage treatment plant was built in 2017, with a daily treatment scale of 10,000 cubic meters. The completion and operation of the sewage treatment plants have reduced the discharge of industrial wastewater and urban domestic sewage, which is conducive to improving the water environment quality in the middle and lower reaches of the Xiali River. Lishi Town and Tianjiu Town, where the Xiali River is located, are the concentrated areas of livestock and poultry breeding and distribution in Dingnan County, and livestock and poultry breeding discharge a large amount of wastewater containing ammonia nitrogen. Since 2016, the local government has carried out a series of livestock and poultry breeding consolidation policies, including waste consolidation in the second half of 2016, livestock and poultry waste recycling use in 2018, and measures to reduce the breeding wastewater discharge, constructing an ecologically friendly modern livestock and poultry breeding industry, which improves the water quality of the Xiali River.

4.3. Suggestions for Water Environment Management of Headwaters in Mountainous

This paper analyzes the spatial-temporal characteristics of water environments and the influence of human activities in the Xiali River basin, which can provide reference for the local water environment management policy and also the headwaters in similar basins of subtropical humid zones. The main pollutants in the local water environment are ammonia nitrogen and total phosphorus, and the former exceeds the Class III according to the state standard of surface water environment quality of China (GB3838-2002). The ammonia nitrogen is positively correlated with the proportion of construction land area. The regression equation of ammonia nitrogen and construction land shows that if the concentration of ammonia nitrogen is controlled at 2 mg/L (Class VI water), the proportion of construction land area is close to 1%. Therefore, it is difficult to meet the local water environment management needs from the land use structure adjustment. It is necessary to reduce the ammonia nitrogen pollution load in the middle and lower reaches of the Xiali

River from the aspects of land use quality, industrial structure upgrading, and ecological environmental management. Li et al. [37] stated that increasing the proportion of green spaces and permeable roads in construction land may control land runoff pollution and improve runoff water quality. The environmental management of the past five years shows that measures such as centralized sewage treatment and large-scale farming will help reduce the discharge of ammonia nitrogen pollutants.

Small river basins in mountainous areas are often located in the upstream or headwaters of rivers, and the river water environment capacity is small [38]. Human activities in the basin have a great impact on the water environment. Because of the steep terrain slope, the area of cultivated land in small watersheds in mountainous area is smaller, and most of it is concentrated in the gully basin, and some of it is located at the foot of gentle slopes or mountain slopes. Current studies reported that there is uncertainty in the relationship between cultivated land and water environments in small watersheds, but there is a significant positive correlation between construction land and water environments [33]. The expansion of construction land reflects human activities such as the increase of population and the operation of industrial and mining enterprises in the basin, which lead to the discharge of urban domestic sewage and industrial wastewater in the basin and drives the increase of pollutants such as nitrogen and phosphorus in the river. Therefore, control of the scale of construction land and the layout of industrial structure should be adopted to reduce river pollution. In addition, controlling the discharge of sewage is also suggested to reduce river pollutant concentrations.

5. Conclusions

This paper analyzed the spatial-temporal characteristics of water quality in a small catchment of headwaters of the Dongjiang River. The influence of human activities exemplified by land use on water quality was also explored based on stepwise regression analysis. The conclusions were:

(1) The water quality of the Xiali River has certain spatial variation characteristics. The water quality in the upper reaches is better than others, while the concentration of organic matter, nitrogen, phosphorus, and fluoride in the middle and lower reaches of the river is relatively high, exceeding the national standard's Class III. The most polluted area are the rivers between the Yangmei River and Dingnan substation, which should demand priority attention.

(2) The principal components and correlation analysis demonstrated that there was a significant correlation between the water quality parameters of the Xiali River. Organic pollutants, nitrogen and phosphorus, and fluoride were the main factors of the water quality parameters of the Xiali River. The PCA analysis results also indicated that they may come from common pollution sources. Dissolved oxygen and pH were negatively correlated with them. The water temperature was negatively correlated with total phosphorus, but not with ammonia nitrogen.

(3) The water quality of the Xiali River showed an improvement trend from 2015 to 2020. Ammonia nitrogen concentrations showed a significant decreasing trend, and total phosphorus concentrations showed a decreasing trend with fluctuation. This is due to the ecological compensation in the upper and lower reaches of the Dongjiang River basin, the centralized treatment of sewage, and the centralized management of livestock and poultry breeding. The major pollutants, i.e., ammonia nitrogen and total phosphorus, have been greatly reduced, and the pollution has been controlled to a certain extent.

(4) Regression analysis results imply the certain relationship between land use and water quality parameters, especially for construction land area, ammonia nitrogen, and total phosphorus concentration. Both ammonia nitrogen and total phosphorus are significantly correlated with construction land area, but ammonia nitrogen is more closely related to construction land area than total phosphorus. Suggestions include controlling the scale of construction land, adjusting the industrial structure, and adopting sewage concentrate treatment to reduce river pollution in the headwaters of the Donjiang River.

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