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River water quality and pollution sources in the Pearl River Delta, China

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Some physicochemical parameters were determined for thirty field water samples collected from different water channels in the Pearl River Delta Economic Zone river system. The analytical results were compared with the environmental quality standards for surface water. Using the SPSS software, statistical analyses were performed to determine the main pollutants of the river water. The main purpose of the present research is to investigate the river water quality and to determine the main pollutants and pollution sources. Furthermore, the research provides some approaches for protecting and improving river water quality. The results indicate that the predominant pollutants are ammonium, phosphorus, and organic compounds. The wastewater discharged from households in urban and rural areas, industrial facilities, and non-point sources from agricultural areas are the main sources of pollution in river water in the Pearl River Delta Economic Zone.

Introduction

The study area, the Pearl River Delta Economic Zone (PRDEZ), is a region full of water channels: the main rivers, tributaries, streams, ditches, and estuaries. The main channel, the Pearl River, is composed of the East River, the West River and the North River. This river system feeds the major rural, agricultural, urban, and industrial areas of the Pearl River Delta and flows into the South China Sea through eight separate river mouths (Fig. 1). The PRDEZ is one of the most developed regions in China. Since the reformation and opening of China in 1978, the PRDEZ has been undergoing the rapid urban expansion and subsequent socio-economic development.

Rapid urban expansion produces negative impacts on the natural environment, especially river water quality. In the PRDEZ, the mean annual local total runoff over many years is 420.5×10^8 m^3; the average annual total runoff over many years (local water plus transient water) is 3362×10^8 m^3. This volume of river runoff is second only to that of the Changjiang River in China. The available *per capita* water quantity in the PRDEZ is about 15 024 m^3. This is approximately 6.7 times as much as the available *per capita* water for the entire country. Moreover, it is 1.7 times as much as the available per capita water for the entire world.[1] The water resource of the PRDEZ is plentiful, yet many cities such as Guangzhou, Shenzhen, Huizhou, and Zhuhai experience water shortages at different periods. As suggested by Dong *et al.*[2] and Zhu *et al.*,[3] one of the main causes for this water shortage is water pollution. Research has been performed on river water quality for the PRDEZ.[4–7]

The primary aim of the present study is not only to examine the river water quality and its main pollutants, but also to investigate the main causes for river water pollution in the Pearl River watershed. The study also provides several approaches for protecting and improving the river water quality for the PRDEZ. Some physicochemical parameters (pH, DO, turbidity, and chroma), organic parameters (COD_{Mn}, TOC), and major nutrient indices (N-NO_2^-, N-NO_3^-, N-NH_4^+, and total phosphorus) were determined for thirty field water samples collected from different locations on the PRDEZ river system. By comparing the analytical results with the environmental quality standards for surface water, the river water quality within the PRDEZ was determined. Wastewater discharge and treatment were considered to determine river water management efficiency.

Materials and methods

Thirty field water samples were collected from the PRDEZ river system for water quality analyses. Both the spatial distribution and the water quality of the river channels were considered in the selection of sample sites. Locations of sampling sites are shown in Fig. 1. All the samples were collected during the middle water level period of the hydrological year 2002. Consequently, these water samples and the analytical results can represent the base flow of the watershed.

As shown in Fig. 1, all the samples can be divided into two groups. Sampling sites 3, 6, 8, 11, 14, 15, 16, 17, 18, 20, 24, 27, and 28 were situated close to or within urban or industrial areas. These samples were regarded as "urban samples" in this study. The water quality of urban samples may have been affected mainly by urban and industrial activities. On the other hand, sampling sites 1, 2, 4, 5, 7, 9, 10, 12, 13, 19, 21, 22, 23, 25, 26, 29, and 30 were located in rural areas. Correspondingly, this group of samples was called "rural samples." The main pollution sources in rural areas are normally agriculture and Township–Village Enterprises. Within the rural samples, sample 21 was located in the estuary of the Pearl River. Some physicochemical parameters such as turbidity might be influenced by seawater for this sample.

Three bottles of water were collected from each sample location. In order to stabilize the oxygen dissolved in water, 1 mL manganese sulfate ($MnSO_4$) and 2 mL alkaline iodized potassium (NaOH–KI) were added to the water for determining dissolved oxygen (DO). Samples for measuring total organic carbon (TOC) and permanganate value (COD_{Mn}) were acidified with H_2SO_4 to bring their pH values below 2.0. A sample of raw water was collected for monitoring the other

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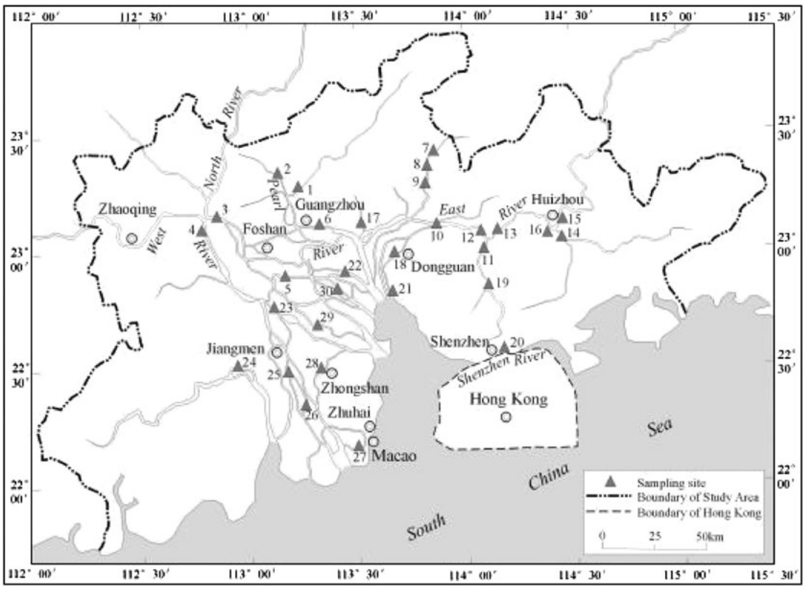

Fig. 1 Study area and sampling sites.

parameters. All samples were transported to the laboratory and analysed within two days.

All the analyses were completed by the primary author and Jianquan Lei at the National Key Laboratory of Organic Geochemistry, Guanghzou Institute of Geochemistry, Chinese Academy of Sciences. The concentrations of total phosphorus were measured using an inductively coupled plasma-mass spectrometer (ICP-MS). Measurement precision was much better than 5% RSD for most of the samples. The average value of all samples was 5.4%. A UV-persulfate TOC analyser (Phoemix 8000) was used to determine the TOC concentrations. Turbidity and chroma were measured colorimetrically as light absorbance at 450 nm (detection limit 5 units), giving the value in NTU (Nephelometric Turbidity Units) and CU (Colour Units), respectively. For both turbidity and chroma, twelve standard solutions were monitored to create biases. Eventually, the monitoring results were determined using the biases for turbidity and chroma respectively. Analytical methods used for other parameters in this study were adopted from ref. 8. If there were several methods for the same parameter introduced in this book, the method cited in the table Analytical Methods of Environmental Quality for Surface Water was selected. Each parameter was analysed at least three times for every sample. Based on these replicate analyses, the precision was calculated for every parameter, they were much better than 2.0% RSD.

The Environmental Quality Standards for Surface Water (GB3838-88) are widely used for assessing water quality in China, and they were used to classify river water in the present research. However, there are no definite standards for TOC, turbidity, and chroma for surface water measurements at present. Nevertheless, turbidity and chroma quality standards for groundwater (GB/T 14848-93) can be used as references. Among the analysed samples, significant positive correlations between TOC and COD_{Mn} (the correlation coefficient was 0.858 in the present research) were observed. However, in seriously contaminated water samples, not all organic compounds could be oxidized by potassium permanganate. Thus, the TOC and COD_{Mn} values in the seriously contaminated samples did not show significant positive correlation. The samples whose COD_{Mn} values were less than the standard for class III were chosen to perform regression analysis between COD_{Mn} and TOC. The regression equation was $y = 0.907x - 0.679$ ($R^2 = 0.930$), where y stands for TOC and x for COD_{Mn}. Based on this regression equation and the COD_{Mn} standards, rough standards for TOC were calculated. The results, as well as the environmental quality standards for the other parameters, are presented in Table 1.

Using the statistical software SPSS, correlation analysis was performed among all the parameters and for the two groups of samples. Factor analysis was performed on the basis of principal component analysis to reduce the influencing factors for both rural and urban samples.

Results and discussion

Our analytical results indicated a reductive circumstance in the river water in the study area. Some distribution characteristics were derived from the analytical results shown in Table 2. In general, the concentrations of nitrate did not exceed the boundary values of class I. Meanwhile, relatively high concentrations of nitrite and nitrate appeared in the rural samples. It

Table 1 Environmental quality standards for surface water (GB3838-88)

Water quality class		I	II	III	IV	V
pH		6.5–8.5	6.5–8.5	6.5–8.5	6.5–8.5	6–9
Nitrate/N mg L^{-1}	≤	10	10	20	20	25
Nitrite/N mg L^{-1}	≤	0.06	0.1	0.15	1.0	1.0
Ammonium/N mg L^{-1}	≤	0.02	0.02	0.02	0.2	0.2
Total P/mg L^{-1}	≤	0.02	0.1	0.1	0.2	0.2
COD_{Mn}/mg L^{-1}	≤	2	4	6	8	10
DO/O_2 mg L^{-1}	≥	Sat 90%	6	5	3	2
TOC/C mg L^{-1a}	≤	1.14	2.95	4.76		

[a] Calculated on the basis of the relationship between COD_{Mn} and TOC.

Table 2 Analytical results for every sample and each parameter (analytical methods are from ref. 12)

Parameter / Sampling no.		pH	$N-NO_2^-$ N/mg L^{-1}	$N-NH_4^+$ N/mg L^{-1}	$N-NO_3^-$ N/mg L^{-1}	DO O_2/mg L^{-1}	Turbidity /NTU	Chroma /CU	COD_{Mn} /mg L^{-1}	TOC C/mg L^{-1}	Total P P/mg L^{-1}
Rural samples	1	6.7	0.003	2.10	1.20	2.4	24	25	5.3	4.10	0.13
	2	6.7	0.002	2.00	1.50	1.2	58	45	5.6	4.20	0.13
	4	7.5	<0.001	0.19	1.00	9.6	29	5	1.5	0.89	0.04
	5	7.4	<0.001	0.40	0.70	9.2	33	15	1.3	0.96	0.05
	7	7.2	<0.001	0.14	0.30	9.5	13	7	1.2	0.62	0.02
	9	7.1	0.009	0.30	0.30	9.3	36	5	1.6	0.78	0.03
	10	6.8	0.001	0.48	0.50	8.4	49	15	1.6	0.92	0.06
	12	6.9	0.001	0.64	0.40	8.8	35	15	1.5	1.10	0.07
	13	7.0	<0.001	0.46	0.40	8.9	34	15	1.5	0.97	0.06
	19	6.6	0.082	0.60	0.40	6.5	40	5	2.7	2.02	0.12
	21	7.4	0.156	0.06	0.02	5.7	92	20	7.5	0.97	0.05
	22	7.4	0.145	<0.02	0.50	6.5	37	5	2.0	1.16	0.09
	23	7.5	0.029	0.04	1.00	7.4	67	20	2.7	0.90	0.04
	25	7.5	0.025	0.12	1.00	7.6	24	5	2.2	1.18	0.04
	26	7.5	0.029	0.08	1.10	7.9	19	5	2.1	1.13	0.05
	29	7.5	0.021	0.06	1.00	8.2	15	<5	2.3	0.92	0.05
	30	7.5	0.076	<0.02	0.95	7.3	20	<5	2.2	1.01	0.06
Urban samples	3	7.3	<0.001	0.18	0.60	10.0	15	10	1.5	0.73	0.02
	6	7.0	<0.001	6.00	0.10	1.2	71	25	5.4	4.80	0.34
	8	6.3	0.006	0.24	0.30	9.3	11	5	1.6	0.66	0.01
	11	6.9	0.001	4.80	2.00	6.3	33	40	6.3	4.50	0.94
	14	6.9	<0.001	4.60	0.40	6.7	40	15	3.1	2.50	0.30
	15	7.3	<0.001	0.12	0.10	9.1	10	5	1.3	0.85	0.02
	16	6.5	<0.001	0.06	0.20	8.1	68	15	1.6	1.50	0.03
	17	7.3	<0.001	30.00	0.02	1.1	67	35	24.0	44.50	2.01
	18	7.0	<0.001	16.00	0.02	0.7	78	30	13.0	5.73	1.48
	20	6.8	<0.001	40.00	0.02	0.4	63	40	29.0	21.70	5.60
	24	6.7	0.114	0.02	1.20	3.5	54	20	3.8	2.80	0.08
	27	7.1	0.069	1.00	0.90	4.5	42	5	3.0	1.81	0.16
	28	7.1	0.040	8.00	0.02	1.6	41	25	7.8	3.48	0.55

can be accounted for by the overuse of nitrogenous fertilizers in agriculture. The pH values of urban samples were generally lower than those of rural samples. Furthermore, the pH value of sample 8 was lower than the quality standard for class II. This result must be due to relatively higher acid deposits within the urban areas. In addition, the DO concentrations of the rural samples were higher than those of the urban samples. As for the other parameters, the concentrations in urban river water bodies were much higher than those in the rural water bodies. Our analytical results indicate that urban waters are more seriously contaminated than rural waters.

Within the rural samples, the results of sample 21 were very abnormal compared to the others. The concentrations of nitrogen parameters had the same characteristics as the other samples. In contrast, the concentration characteristics of the other parameters were very different from the other samples. Specifically, the result for COD_{Mn} was much higher than the standard of class II, while the concentrations of TOC and total P were very low. Moreover, the result for turbidity was excessively high. All these abnormalities could be, most likely, due to the influence of seawater. In sample 30, as seen from the analytical results, the concentrations of all analytical parameters were within the standards of class II. For the urban samples, samples 3, 8, 15, and 16, were relatively clean except that the ammonium concentrations were a little higher than the standards of class II. Conversely, river water of samples 17, 18, and 20 were contaminated very seriously. The concentrations of $N-NH_4^+$, COD_{Mn}, TOC, and total P were extremely high compared to the environmental quality standards for surface water listed in Table 1. In samples 18 and 20, the concentrations of DO were less than 1.0. The highest concentration of TOC, 44.50 mg L^{-1}, appeared in sample 17, while the highest concentrations of $N-NH_4^+$, COD_{Mn}, and total P, 40.00 mg L^{-1}, 29.0 mg L^{-1}, and 5.60 mg L^{-1}, respectively, appeared in sample 20. Excluding sample 21, sample 18 had the highest turbidity, 78 NTU. These three samples (17, 18 and 20) were located within Guangzhou, Dongguan, and Shenzhen metropolitan areas, respectively. Concentrated urban and industrial activities in these areas account for the high pollutant concentrations in these samples.

Correlation analysis was performed for the two groups of samples separately using the analytical results listed in Table 2. According to the results of the correlation analysis, at a 95% significance level, pH, nitrite, and nitrate are independent and have no correlation with the other parameters for urban samples. Unlike urban samples, only nitrite is independent for rural samples. Significant positive or negative correlations exist between any two other parameters. On the basis of these relationships, it can be thought that a few factors can explain the main variance of these ten parameters, and that the data set can be reduced using principal component analysis and factor analysis. The main pollutants for river water in the study area can be determined from these statistical analyses. The eigenvalues of the principal component analysis are illustrated in Fig. 2.

Usually, the eigenvalue 1.0 is a critical value for principal component analysis, and the principal components whose eigenvalues are equal to and larger than 1.0 can explain most of the total variance. From Fig. 2, four principal components can represent the ten parameters of all samples. Meanwhile, three principal components can explain most of the total variance for both rural samples and urban samples. Therefore, factor analysis was performed on the basis of principal component analysis. The total explained variance of the first four components is more than 87.4% for all samples. The numbers for the first three components are 78.5% for urban samples and

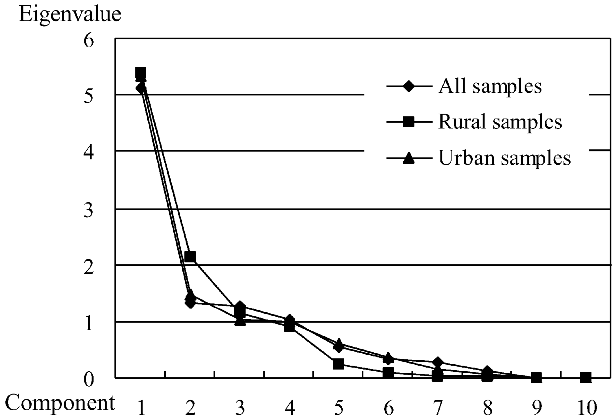

Fig. 2 Eigenvalues of principal component analysis.

86.8% for rural samples. Furthermore, the results of the component matrix and the component score coefficient matrix for rural and urban samples are shown in Table 3.

From Table 3, it is found that the parameters ammonium, total P, DO, chroma, COD_{Mn}, and TOC cluster in the first component for both the rural and urban samples. The turbidity within the urban samples has the same clustering characteristic. Therefore, it can be concluded that the main pollutants in the study area are ammonium, phosphorus, and organic compounds. At the same time, the pollutants influence the appearance of the river water. Nitrite and turbidity are the main parameters represented by the second factor for rural samples, while nitrite and nitrate cluster to the second component for urban samples. The third component is mainly characterized by pH for both sub-sets, and nitrate for rural samples, as well.

Comparisons were performed between the analytical results and the environmental quality standards for surface water listed in Table 1. The percentage of river water samples worse than class II is listed in Table 4 for the rural and urban samples. Choosing the lowest class for all parameters of each sample as the class for that sample, only river water in sampling site 30 reaches class II and can be used as a drinking water source. The quality of the other twenty-nine water samples is worse than class III.

From Table 4, it can be seen that the river water of the study area is not contaminated by nitrate. Acid and alkali pollution appears in some urban river water bodies, but it can be neglected for rural river waters. For nitrite, the percentage of the rural samples worse than class II is a little higher than that of the urban samples. Fortunately, the percentages are very low. Therefore, the nitrite pollution is not too serious. As for the other parameters, the percentages of the urban samples worse than class II are much larger than those of the rural samples. Surprisingly, most of the ammonium concentrations exceed the upper boundary values of class II. The percentages of samples worse than class II are 88.2% and 92.3% for the rural samples and the urban samples, respectively. Obviously, the river water suffers serious ammonium pollution in the study area, while less than 20% of the rural samples were worse than class II for P, DO, COD_{Mn}, and TOC. According to these parameters, the water pollution in rural rivers is not as serious as in urban rivers. The percentages of urban samples with COD_{Mn} and TOC levels exceeding class II are less than but very close to 50%. Furthermore, the concentrations of total P and DO exceed the boundaries of the standards of class II for more than half of the urban samples. These percentages indicate that urban waters are very low in quality. Comparing the analytical results to the quality standards for groundwater, turbidity results exceed the boundary values of class II for all the water samples. Regarding chroma, only samples 29 and 30 reach the standard of class II. The water pollution directly influences the appearance of river water in both rural and urban areas.

Table 4 Percentage of river water samples worse than class II (%)

Parameters	Rural samples	Urban samples
pH	0.0	7.7
$N\text{-}NO_2^-$	11.8	7.7
$N\text{-}NH_4^+$	88.2	92.3
$N\text{-}NO_3^-$	0.0	0.0
Total P	17.6	61.5
DO	17.6	53.8
COD_{Mn}	17.6	46.2
TOC	11.8	46.2

Considering the findings, the river water is of low quality in the study area. The reasons for the serious pollution may come from two sources.

Firstly, large municipal and industrial discharge and agricultural production plays a main role in the river water quality. Chen *et al.* also discussed this cause when they studied the human influences on nitrogen contamination in the Yellow River system in China.[9] Furthermore, the research of Ferrier *et al.* indicated that relationships existed between nitrate concentrations and agriculture and also between urban catchments and ammonium and phosphorus for rivers in Scotland.[10] In Spain, it was also found that increases in human activities caused high levels of nutrients in river water.[11] According to the Bureau of Environmental Protection, Guangdong Province, a large amount of waste is discharged into rivers in the PRDEZ every year.[12] The quantities of wastewater and the COD quantities within the wastewater discharge for the whole PRDEZ are illustrated in Fig. 3.

Table 3 Component matrix and component score coefficient matrix for rural and urban samples

Matrix	Component matrix						Component score coefficient matrix					
Sample-set	Rural samples			Urban samples			Rural samples			Urban samples		
Component	1	2	3	1	2	3	1	2	3	1	2	3
pH	−0.661	0.191	0.704	0.188	−0.301	0.904	−0.123	0.089	0.609	0.035	−0.205	0.870
$N\text{-}NO_2^-$	−0.040	0.852	0.144	−0.233	0.794	0.240	−0.007	0.398	0.124	−0.044	0.540	0.231
$N\text{-}NH_4^+$	0.924	−0.311	−0.147	0.970	−0.125	−0.032	0.172	−0.145	−0.127	0.182	−0.085	−0.031
$N\text{-}NO_3^-$	0.447	−0.509	0.702	−0.361	0.589	0.217	0.083	−0.238	0.607	−0.068	0.401	0.209
Total P	0.863	−0.037	−0.121	0.873	−0.055	−0.158	0.160	−0.017	−0.105	0.163	−0.037	−0.152
DO	−0.940	−0.163	−0.227	−0.809	−0.389	−0.107	−0.175	−0.076	−0.196	−0.151	−0.264	−0.103
Turbidity	0.330	0.790	−0.113	0.676	0.378	−0.197	0.061	0.369	−0.098	0.127	0.257	−0.190
Chroma	0.845	0.078	0.001	0.819	0.263	0.008	0.157	0.036	0.001	0.153	0.179	0.008
COD_{Mn}	0.715	0.575	0.204	0.975	−0.048	0.008	0.133	0.268	0.176	0.183	−0.033	0.008
TOC	0.964	−0.190	0.077	0.826	−0.138	0.200	0.179	−0.089	0.067	0.155	−0.094	0.192

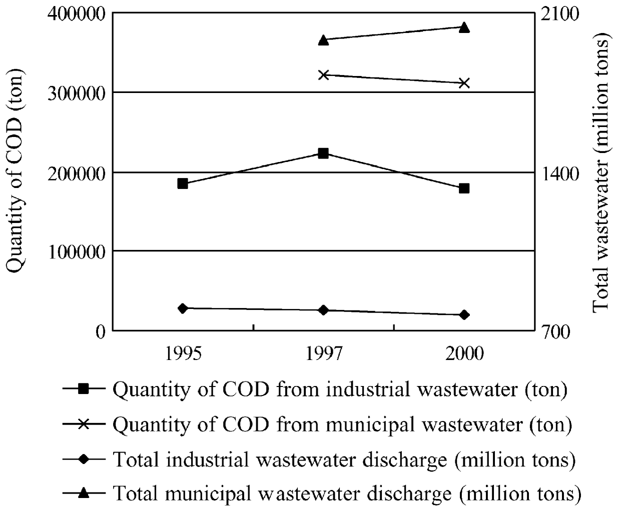

Fig. 3 Wastewater and COD discharge from the PRDEZ.

Fig. 3 shows that the discharge of total industrial wastewater stayed stable or showed a slightly decreasing trend in the study area from 1995 to 2000, but the total quantity of industrial wastewater discharged was still very large. The quantity of COD within this industrial wastewater varied greatly. On average, about 786.3 million tons of industrial wastewater with 195 540 tons of COD was discharged into the environment each year. As for municipal wastewater discharge, a slightly increasing trend appeared from 1997 to 2000. The quantity of COD from municipal wastewater stayed constant, but it was much more than that from industrial wastewater. The annual discharge of municipal wastewater was 2007.8 million tons. Within this wastewater, 317 191 tons of COD were discharged into the environment each year. This discharge of COD accounts for the high concentration of COD_{Mn}. On the other hand, the percentage of discharged industrial wastewater that matches the environmental quality standard for industrial discharge increased year by year. Therefore, it appears that the industrial contamination of river water is coming under control. However, municipal wastewater was not effectively treated before discharging. Therefore, while industrial pollution is no doubt an influencing factor for river water pollution, municipal wastewater discharge has become the main source of river water pollution.

Secondly, low percentages of wastewater treatment and low runoff must be another reason. For example, Shenzhen River, a very small stream located between Shenzhen and Hong Kong, is the only watershed within Shenzhen city. Low self-purification, large wastewater discharge, as well as deficient management cause serious contamination of the Shenzhen River. Similarly, Ibe and Njemanze found that untreated sewage is one of the most important sources of contamination in Nigeria.[13]

As for rural rivers, agricultural production may be the source of nitrogenous compounds. At the same time, organic compounds have also become major pollutants in rural river waters. The causes for this result can be traced as follows.

Wastewater that comes from Township-Village Enterprises is a significant pollution source. Lack of planning in the layout of the Township-Village Enterprises and non-treatment of the wastes discharged from the factories aggravated the river water pollution. Moreover, some contaminative industries moved from the urban to the rural area during urban development. That is to say, if the study area is regarded as a whole, the area of pollution was extended.

In the PRDEZ, the income of peasants has reached relatively high levels in China. For example, in 1999, the average income of urban households was about 1500 US dollars *per capita*; however, the *per capita* income of relatively higher-earning rural households was one US dollar higher than that of urban residents in Guangzhou.[14] With the improvement in rural life, the consumptive structure of the peasants became very similar to that of the urban residents. Most electrical and chemical products entered the rural household, and the diet of the rural family changed greatly. Consumption of these products added many inorganic and organic pollutants to the rural sewage. As a result, the ingredients of rural wastewater became more and more complex. Furthermore, most of this wastewater was discharged directly into the river without any treatment. Therefore, rural wastewater became one of the most serious pollution sources. As reported by Robson and Neal, sewage effluent was regarded as one of the most significant point sources of many pollutant chemicals in a Scottish rural river system, the Tweed basin.[15]

In addition, in order to promote the productivity of agricultural land, more and more chemical fertilizers and pesticides have been used. For example, the chemical fertilizer input per cultivated land area of 1997 was more than three times as much as that of 1980 in Guangzhou.[16] These fertilizers and pesticides produced not only inorganic pollutants but also organic matter that is difficult to decompose. Furthermore, the agricultural wastewater was discharged into rivers without any treatment. Therefore, agricultural pollution has also had a serious impact on river water quality.

Conclusions

Generally, the river water of the study area is of low quality and in a reductive circumstance. Ammonium, phosphorus, and organic compounds are the most predominant pollutants. These pollutants come from industry, daily life, and agriculture. Municipal wastewater is the greatest pollution source for urban rivers. As for rural rivers, Township-Village Enterprises, agriculture, and rural daily living all contribute to the water pollution.

The causes of serious water pollution include the following factors: urban and rural sewage is the largest pollution source to river water. Industrial wastewater is another serious pollution source. In addition, chemical fertilizers and pesticides used in agriculture introduce direct pollution to rural river water.

As a significant water resource of the PRDEZ, the river water quality must be protected and improved as soon as possible. The following measures are suggested as necessary approaches for protecting and improving river water quality. First of all, the treatment of industrial wastewater must be enforced continuously, and urban and rural sewage must be treated before discharging. Second, planning the layout of the Township-Village Enterprises rationally and reducing the waste discharge from factories is another effective approach. Third, enforcing agricultural management is the main way to reduce pollutions in rural river waters. Finally, increasing investment in environmental management and controlling the expansion of industrial facilities are important for the improvement of the river water quality.

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