Spatial and Seasonal Patterns of Nutrients and Heavy Metals in Twenty-Seven Rivers Draining into the South China Sea

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Abstract: Due to the acceleration of industrialization and urbanization in recent decades, the majority of coastal rivers and estuaries in China have been moderately or severely contaminated by a variety of pollutants. We investigated the spatial and seasonal variations of water nutrients (permanganate index, chemical oxygen demand, biochemical oxygen demand, ammonium, nitrate, total nitrogen, and total phosphorus) and heavy metals (Hg, Pb, Cu, Zn, Se, As, Cd, Cr, Fe, and Mn) in 27 subtropical rivers draining into the South China Sea. Our results indicated that the average concentrations of all water quality parameters except ammonium, total nitrogen, and total phosphorus satisfied the requirements for grade III of the surface water quality standard of China. The concentrations of both nutrients and heavy metals showed a strong spatial variation. Cluster analysis classified the 27 rivers into three spatial clusters corresponding to low, moderate, and high pollution levels. In terms of seasonal variation, the values of chemical oxygen demand and biochemical oxygen demand in wet seasons were significantly lower than those in dry seasons. Multivariate statistical analyses demonstrated that river nutrients might mainly originate from domestic, industrial, and agricultural wastewaters, while heavy metals likely came from industrial activities and natural weathering processes. The findings of this study suggest that for reducing the pollution of subtropical rivers draining into the South China Sea, further efforts should be made to control nitrogen and phosphorus export from catchments.

Keywords: nitrogen; phosphorus; source identification; trace metals; water quality

1. Introduction

Water quality plays a critical role in determining the ecological conditions and functions of aquatic habitats [1,2]. Excess nutrients and heavy metals in rivers are considered to be the major environmental problems in many countries, and especially in China [3–6]. Eutrophication, characterized by excessive growth of algae and other aquatic plants, is a common consequence of nitrogen (N) and phosphorus (P) enrichment in rivers and streams [7,8]. Water quality degradation can also result in many other ecological problems such as a reduction of aquatic biodiversity, the mortality of benthic communities, and fish deaths [9,10]. In addition, heavy metals can accumulate in the human body via the food chain and lead to serious damage to the nervous system and internal organs [11–14].

Increased delivery of nutrients and heavy metals to coastal oceans through river channels has been recognized as a major threat to the structure and function of continental shelf ecosystems [15]. N and P pollution is now the largest environmental issue in the estuaries and coastal areas of several countries (e.g., the United States and China) and is likely to increase due to intensive use of inorganic fertilizers and fossil fuels [16,17]. In China, the coastal waters have received a large amount of nutrients and heavy metals from rivers because of the rapid economic development and population growth during the past 30 years [18]. A recent study has indicated that the risk for harmful algal blooms in the coastal seas of China may increase in the next half-century due to eutrophication [19].

Nutrients and heavy metals enter the river waters from a wide range of anthropogenic and natural sources in the catchments, such as industrial effluent, domestic sewage, and agricultural runoff [9,20]. Identifying the possible sources of nutrients and heavy metals in river waters is essential for developing a targeted strategy to reduce the negative effects of pollutants on environments and organisms. In the last two decades, multivariate statistical techniques, such as cluster analysis (CA), principal component analysis (PCA), and correlation analysis, have been frequently employed to investigate the spatial–temporal variations of water quality and to identify the possible sources of pollutants in river waters [21–24].

The South China Sea is one of the largest marginal seas in the world, with a surface area of 3.5×10^6 km^2 [25]. There are a large number of subtropical rivers draining into the South China Sea in the province of Guangdong, where industrialization and urbanization have reached high levels [19]. However, until now, few studies have been performed to investigate the spatial and seasonal variations of water quality in these subtropical rivers of South China [26,27]. In this study, we determined the concentrations of 17 nutrient and heavy metal parameters in 27 rivers draining into the South China Sea for every month in 2015. We presented a hypothesis that water quality in rivers might show a significant spatial variation because of differences in catchment characteristics such as industrial development and urbanization. We also hypothesized that due to the dilution effect caused by rainfall and flooding, the concentrations of both nutrients and heavy metals in wet seasons would be significantly lower than those in dry seasons. The objectives of this study were (1) to assess the overall water quality of the studied rivers; (2) to explore the spatial and seasonal pattern of nutrients and heavy metals in river waters; and (3) to examine the possible sources of nutrients and heavy metals using multivariate statistical analyses.

2. Materials and Methods

2.1. Study Area

In the Guangdong province of China, there are 1314 rivers and streams, many of which belong to the Pearl River basin and finally enter into the South China Sea (Figure 1). These rivers and streams play an important role in providing fresh water for industrial, domestic, and agricultural uses in rural areas and cities such as Guangzhou, Shenzhen, and Hong Kong. However, the water quality of these rivers and streams has deteriorated considerably in recent decades and shows strong spatial and temporal variations [26,27] due to rapid economic growth and urban development in catchments. The government report has shown that water pollution is still a serious problem in the Guangdong province and approximately 22.6% of river sections have a water quality worse than Grade III of the environmental quality standards for surface water in China [28].

In 2015, the Guangdong province had a gross domestic product (GDP) of 1169 billion US Dollars and a population of approximately 107 million people. The Guangdong province is characterized by a subtropical monsoon climate, where the annual average temperature is about 21.8 °C. The mean annual precipitation in these areas is over 1789 mm, and approximately 85% of the total rainfall is concentrated in the rainy season from April to September. In the coastal areas of Guangdong province, the topography is relatively flat and the land use is predominantly industrial and urban [29]. After the

opening and reform policy in the late 1970s, the coastal areas have developed faster than the inland regions and have become one of the most developed areas in China.
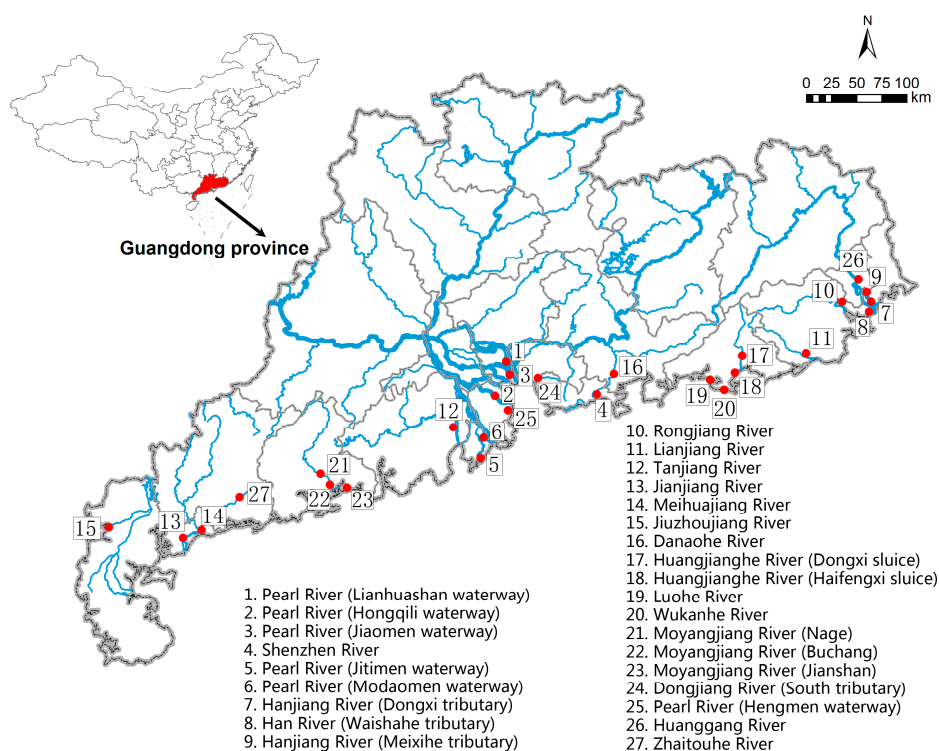

1. Pearl River (Lianhuashan waterway)
2. Pearl River (Hongqili waterway)
3. Pearl River (Jiaomen waterway)
4. Shenzhen River
5. Pearl River (Jitimen waterway)
6. Pearl River (Modaomen waterway)
7. Hanjiang River (Dongxi tributary)
8. Han River (Waishahe tributary)
9. Hanjiang River (Meixihe tributary)
10. Rongjiang River
11. Lianjiang River
12. Tanjiang River
13. Jianjiang River
14. Meihuajiang River
15. Jiuzhoujiang River
16. Danaohe River
17. Huangjianghe River (Dongxi sluice)
18. Huangjianghe River (Haifengxi sluice)
19. Luohe River
20. Wukanhe River
21. Moyangjiang River (Nage)
22. Moyangjiang River (Buchang)
23. Moyangjiang River (Jianshan)
24. Dongjiang River (South tributary)
25. Pearl River (Hengmen waterway)
26. Huanggang River
27. Zhaitouhe River

Figure 1. The sampling locations of 27 subtropical rivers draining into the South China Sea.

2.2. Water Sampling and Analytical Methods

An environmental monitoring system has been set up to monitor the water quality and pollutant fluxes of 27 large rivers draining into the South China Sea in the Guangdong Province. For each river, we established one monitoring station at a site near the river mouth (Figure 1). Replicated samples of surface water (approximately 0.5 m depth) were collected monthly from January to December 2015 in the channel center from a boat or by wading if the water depth was less than 1 m. Pre-treatment methods including acidification and filtration have been described in detail in our previous study [11]. For the purpose of this study, the monthly data of 17 nutrient and heavy metal variables from 27 monitoring rivers during 2015 were determined. The nutrient parameters included permanganate index (I_{Mn}), chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD_5), ammonium (NH_4^+), nitrate (NO_3^-), total nitrogen (TN), and total phosphorus (TP). The heavy metal variables included mercury (Hg), lead (Pb), copper (Cu), zinc (Zn), selenium (Se), arsenic (As), cadmium (Cd), chromium (Cr), iron (Fe), and manganese (Mn).

The nutrient parameters and heavy metal variables were determined in the laboratory using standard methods recommended by the State Environmental Protection Administration of China. The specific method used to determine nutrient parameters is presented as follows: I_{Mn}, acidic potassium permanganate method; COD, Dichromate method; BOD_5, dilution and seeding method; NH_4^+, salicylic acid method; NO_3^-, phenol disulfonic acid method; TN, alkaline potassium persulfate digestion method; and TP, ammonium molybdate method. The Hg and As concentrations were determined by cold atomic fluorescence spectrometry, while the levels of Pb, Cu, Zn and Cd were measured by atomic absorption spectrophotometry. The Se and Cr concentrations were measured using the graphite furnace atomic absorption spectrometric method and the diphenylcarbohydrazide spectrophotometric method, respectively. In addition, the Fe and Mn concentrations were measured by

the flame atomic absorption spectrometric method. The details of these methods have been described elsewhere [11,30]. The detection limits or accuracy of these standard methods have been given in the environmental quality standards for surface water in China (GB3838-2002). For instance, the detect limits of Zn and Pb were 0.05 and 0.01 mg/L, respectively.

2.3. Statistical Analyses

We checked the data for normal distributions using the Shapiro–Wilk test before statistical analyses. Non-normally distributed data were subjected to logarithmic or square root transformations. To evaluate the overall water quality of these studied rivers, we used the environmental quality standards for surface water in China (GB3838-2002) which divided the water quality into five grades (I–V) in accordance with the environmental functions and protective objectives [31]. The grades I and V corresponded to the best and worst water quality, respectively. The grade III was frequently used in assessing the water quality in China [31] because it indicated the water was suitable for fish, aquaculture, and swimming.

Hierarchical cluster analysis (CA) using the squared Euclidean distance was applied to group the 27 studied rivers into several spatial clusters by the similarity of water quality parameters [4]. To examine the seasonal pattern of river water quality, we classified the 12 months into wet season (from April to September) and dry season (from October to the next March) according to monthly precipitation in Guangdong Province. Differences in the nutrient and heavy metal concentrations between spatial clusters and between the sampling seasons were investigated by independent-samples *t*-tests.

Principal component analysis (PCA) using the varimax rotation method was used to identify the possible sources of nutrients and heavy metals in river waters [3,32]. The number of principal components was selected based on Kaiser's rule, which only retained eigenvectors with an eigenvalue greater than one [4]. In addition, relationships between nutrient and heavy metal concentrations were assessed by Pearson correlation analysis, which was also widely used to determine the possible sources of pollutants [33]. The software PASW Statistics 18 (IBM SPSS Inc., Chicago, IL, USA) was used to perform the above statistical analyses.

3. Results

3.1. Overall Assessment of River Water Quality

According to the environmental quality standards for surface water in China, the mean values of most of the water quality parameters in 27 rivers were lower than the values of grade III of the national standard (Table 1). In terms of nutrients, the averages of I_{Mn}, COD, and BOD_5 were 4.49, 18.1, and 3.68 mg/L, respectively, which were slightly lower than the corresponding values of grade III (Table 1). However, the mean concentration of NH_4^+ (1.11 mg/L), TN (2.94 mg/L), and TP (0.22 mg/L) in river water were approximately 1.10, 2.94, and 1.10 times higher than the threshold values of grade III water quality (Table 1).

The average concentrations of all heavy metals satisfied the grade III of the surface water quality standard of China (Table 1). For highly toxic heavy metals, the mean contents of Hg, Pb, As, Cd, and Cr were 0.04, 2.39, 2.72, 0.50, and 4.06 μg/L, respectively, which were about 2.5–21 times lower than the threshold values of grade III water quality (Table 1). However, it should be noted that the maximum value of Fe (492 μg/L) and Mn (430 μg/L) greatly exceeded the limit values for centralized drinking water sources in China (Table 1).

Table 1. Summary statistics of nutrient and heavy metal concentrations in surface water of subtropical rivers (N = 27), and environmental quality standard for surface water in China.

Water Quality Parameters	Abbr	Median	Mean ± SD	Max	Min	Environmental Quality Standard [a]
Nutrients (mg/L)						
Permanganate index	I_{Mn}	3.32	4.49 ± 5.17	45.0	0.50	6
Chemical oxygen demand	COD	12.4	18.1 ± 22.3	201	5.00	20
Biochemical oxygen demand	BOD_5	2.04	3.68 ± 6.43	61.8	0.50	4
Ammonia	NH_4^+	0.28	1.11 ± 2.42	15.8	0.00	1.0
Nitrate	NO_3^-	1.17	1.35 ± 1.19	9.55	0.06	10 [b]
Total nitrogen	TN	2.15	2.94 ± 3.28	24.1	0.35	1.0
Total phosphorus	TP	0.09	0.22 ± 0.44	3.34	0.02	0.2
Heavy metals (µg/L)						
Mercury	Hg	0.04	0.04 ± 0.02	0.11	0.01	0.10
Lead	Pb	1.00	2.39 ± 3.39	22	0.05	50
Copper	Cu	1.30	3.94 ± 9.06	93	0.1	1000
Zinc	Zn	9.78	20.6 ± 20.8	100	0.5	1000
Selenium	Se	0.50	1.27 ± 1.52	11.3	0.09	10
Arsenic	As	1.60	2.72 ± 2.51	7	0.2	50
Cadmium	Cd	0.65	0.50 ± 0.40	1	0.02	5.0
Chromium	Cr	4.00	4.06 ± 0.76	12	2	50
Iron	Fe	86.7	110 ± 90.9	492	1.5	300 [b]
Manganese	Mn	10.0	36.2 ± 62.4	430	0.3	100 [b]

Notes: [a] Grade III of the environmental quality standards for surface water in China (GB 3838-2002). [b] The limit values for centralized drinking water sources in China.

3.2. Spatial Variations in River Water Quality

The spatial patterns of the water nutrients are shown in Figure 2. The highest values of I_{Mn} (25.1 mg/L), COD (112 mg/L), and BOD_5 (30.1 mg/L) were all found in site 11 (Lianjiang River). The spatial patterns of N-related parameters in river water were relatively complex (Figure 2). The highest concentrations of water NH_4^+ (8.84 mg/L) and NO_3^- (2.66 mg/L) were detected in site 11 (Lianjiang River) and site 24 (Dongjiang River south tributary), respectively, while the maximum TN concentration (11.9 mg/L) occurred in site 4 (Shenzhen River).
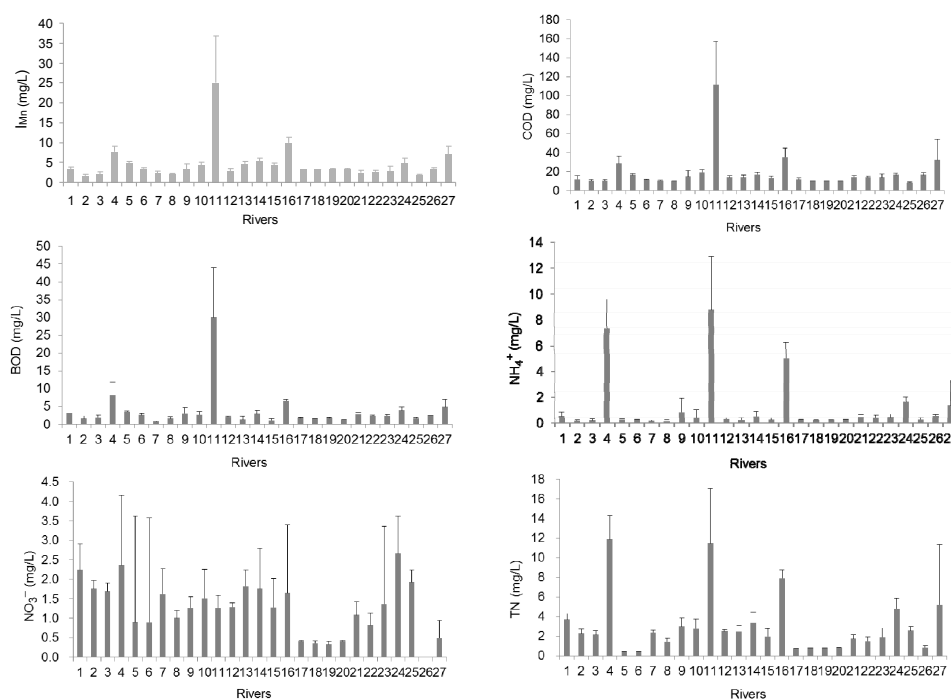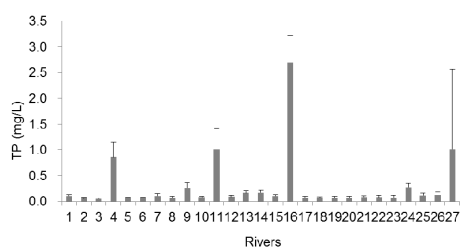

Figure 2. *Cont.*

Figure 2. Spatial patterns of water nutrients (mean ± SD) in 27 subtropical rivers, China. River names are given in Figure 1.

For heavy metals, the highest concentrations of Hg (0.07 µg/L), Fe (232 µg/L), and Mn (184 µg/L) were all found in site 11 (Lianjiang River; Figure 3). In addition, the largest values of Cu (22.0 µg/L), Zn (61.0 µg/L), and Cr (5.33 µg/L) were found in site 16 (Danaohe River), site 23 (Moyangjiang River) and site 6 (Pearl River Modaomen waterway), respectively. Hierarchical cluster analysis classified the 27 river sites into three spatial clusters (Figure 4), corresponding to the low, moderate, and high pollution levels, respectively. All water nutrient parameters (except NO_3^- concentration) in cluster B were significantly higher than those in cluster A (Table 2).
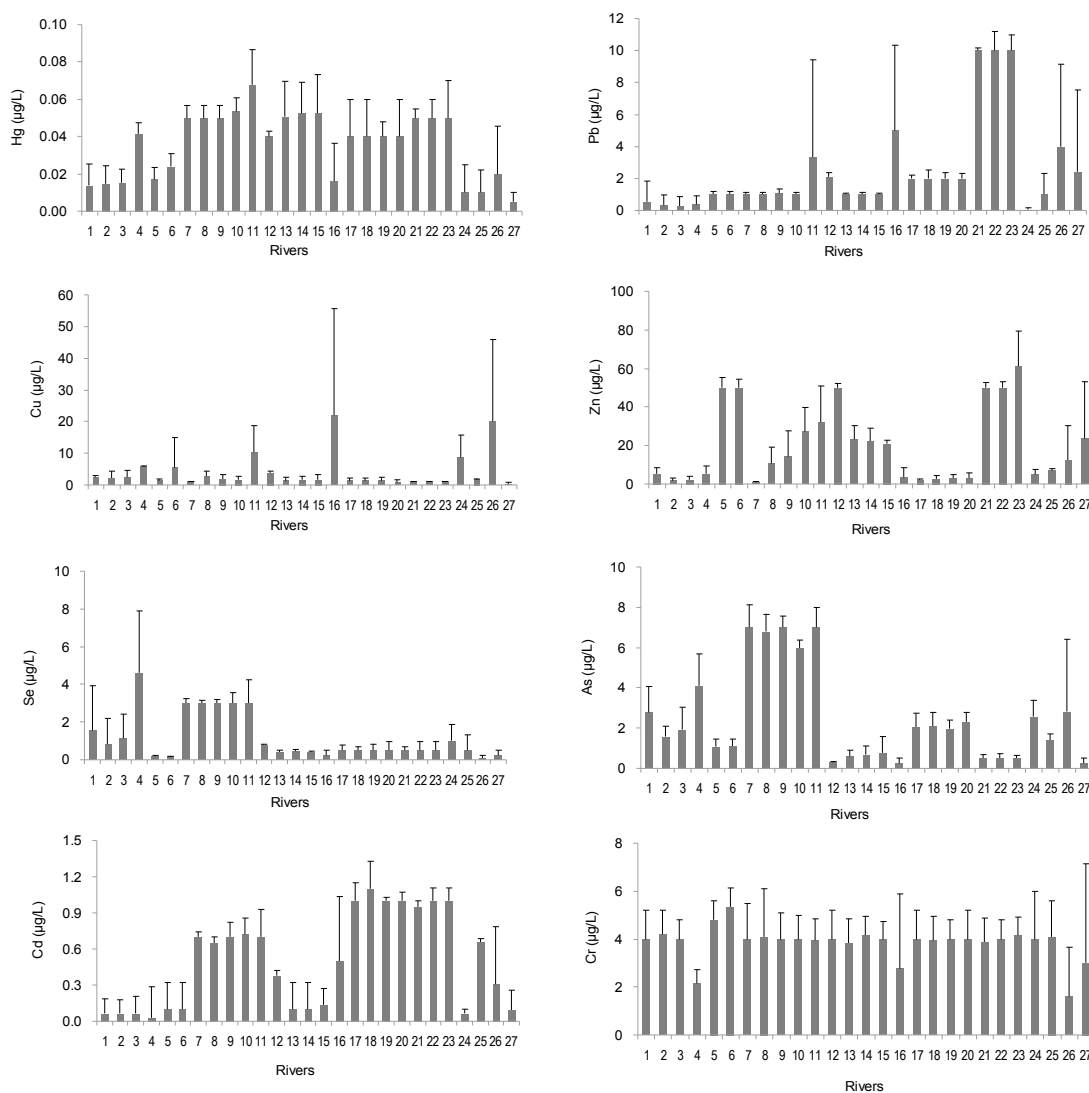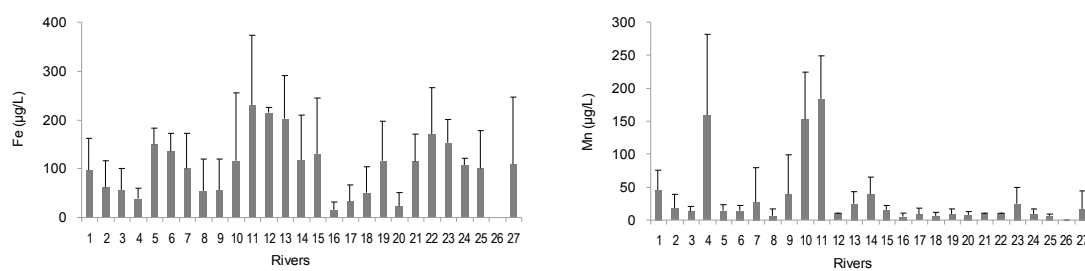

Figure 3. *Cont.*

Figure 3. Spatial patterns of water heavy metals (mean ± SD) in 27 subtropical rivers, China. River names are given in Figure 1.
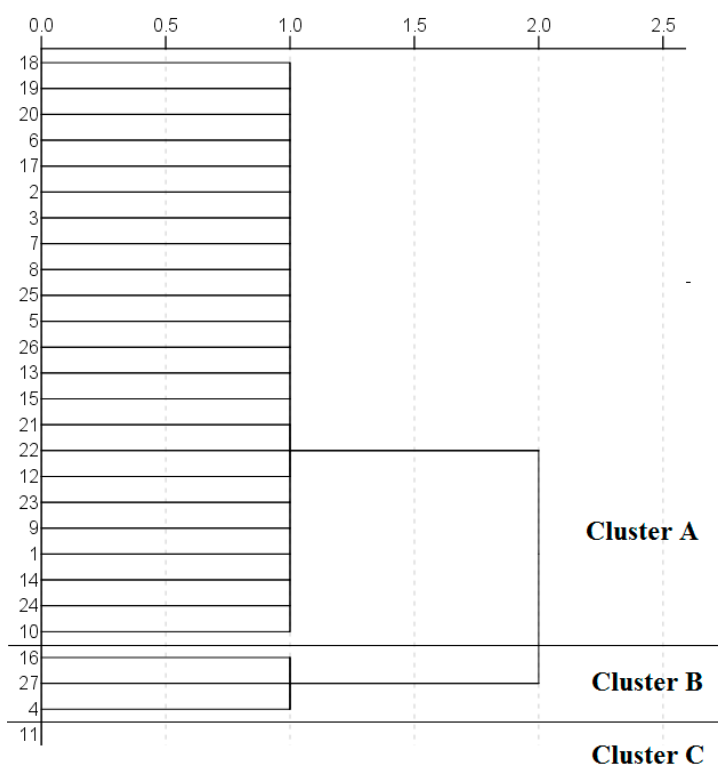

Figure 4. Dendrogram from spatial cluster analysis based on water quality parameters for 27 subtropical rivers, China. River names are given in Figure 1.

Table 2. Statistical test (*t*-test) results of river nutrient and heavy metal concentrations between two spatial clusters as well as between two seasons.

Water Quality Parameters	Cluster A (N = 23)	Cluster B (N = 3)	Cluster C (N = 1)	Dry Season (N = 6)	Wet Season (N = 6)
Nutrients (mg/L)					
I_{Mn}	3.23 ± 1.05 *	8.26 ± 1.52 *	25.1	4.89 ± 0.83	4.18 ± 0.25
COD	12.8 ± 2.83 *	31.8 ± 3.34 *	112	19.9 ± 2.95 *	16.5 ± 1.23 *
BOD_5	2.18 ± 0.82 *	6.48 ± 1.64 *	30.1	4.21 ± 0.86 *	3.26 ± 0.45 *
NH_4^+	0.40 ± 0.33 *	4.59 ± 3.00 *	8.84	1.25 ± 0.34	1.00 ± 0.35
NO_3^-	1.24 ± 0.67	1.50 ± 0.94	1.26	1.43 ± 0.28	1.29 ± 0.33
TN	1.96 ± 1.13 *	8.32 ± 3.37 *	11.5	3.22 ± 0.66	2.72 ± 0.54
TP	0.11 ± 0.06 *	1.52 ± 1.02 *	1.00	0.23 ± 0.08	0.21 ± 0.07
Heavy metals (µg/L)					
Hg	0.04 ± 0.02	0.02 ± 0.02	0.07	0.03 ± 0.00 *	0.04 ± 0.00 *
Pb	2.41 ± 3.12	2.61 ± 2.31	3.33	2.01 ± 0.67	2.47 ± 0.60

Table 2. *Cont.*

Water Quality Parameters	Cluster A (N = 23)	Cluster B (N = 3)	Cluster C (N = 1)	Dry Season (N = 6)	Wet Season (N = 6)
Cu	2.97 ± 4.11	9.43 ± 11.26	10.3	4.32 ± 1.35	3.34 ± 1.48
Zn	20.7 ± 20.49	10.9 ± 11.2	32.2	18.9 ± 2.42	20.5 ± 2.11
Se	1.00 ± 0.99	1.71 ± 2.53	3.00	1.34 ± 0.38	1.11 ± 0.13
As	2.41 ± 2.28	1.53 ± 2.22	7.00	2.66 ± 0.36	2.58 ± 0.26
Cd	0.52 ± 0.40	0.21 ± 0.25	0.70	0.45 ± 0.08	0.51 ± 0.04
Cr	3.99 ± 0.61 *	2.64 ± 0.43 *	4.00	3.85 ± 0.19	3.90 ± 0.25
Fe	103 ± 55.5 *	54.3 ± 48.7 *	232	110 ± 24.7	101 ± 15.1
Mn	22.3 ± 30.8 *	60.4 ± 85.4 *	184	37.4 ± 14.0	32.9 ± 4.45

Note: Mean ± SD followed by an asterisk indicates a significant difference ($p < 0.05$) between cluster A and B or between wet season (from April to September) and dry season (from October to next March).

3.3. Seasonal Variations in River Water Quality

In general, the mean concentrations of most of the nutrient variables were relatively high in the first 3–4 months of the year, and then experienced a gradual decrease in the following months (Figure 5). However, the temporal patterns of NO_3^- and TP concentrations were relatively irregular and complex, with the largest values found in August and January, respectively. For the heavy metals, the contents of all heavy metals (except Pb, Cu, and Mn) were relatively stable over the one-year period (Figure 6). The COD and BOD_5 values in the wet season (from April to September) were significantly lower than those in the dry season (from October to the next March; Table 2). For heavy metals, only the Hg concentration had a significant difference between the wet and dry seasons (Table 2).
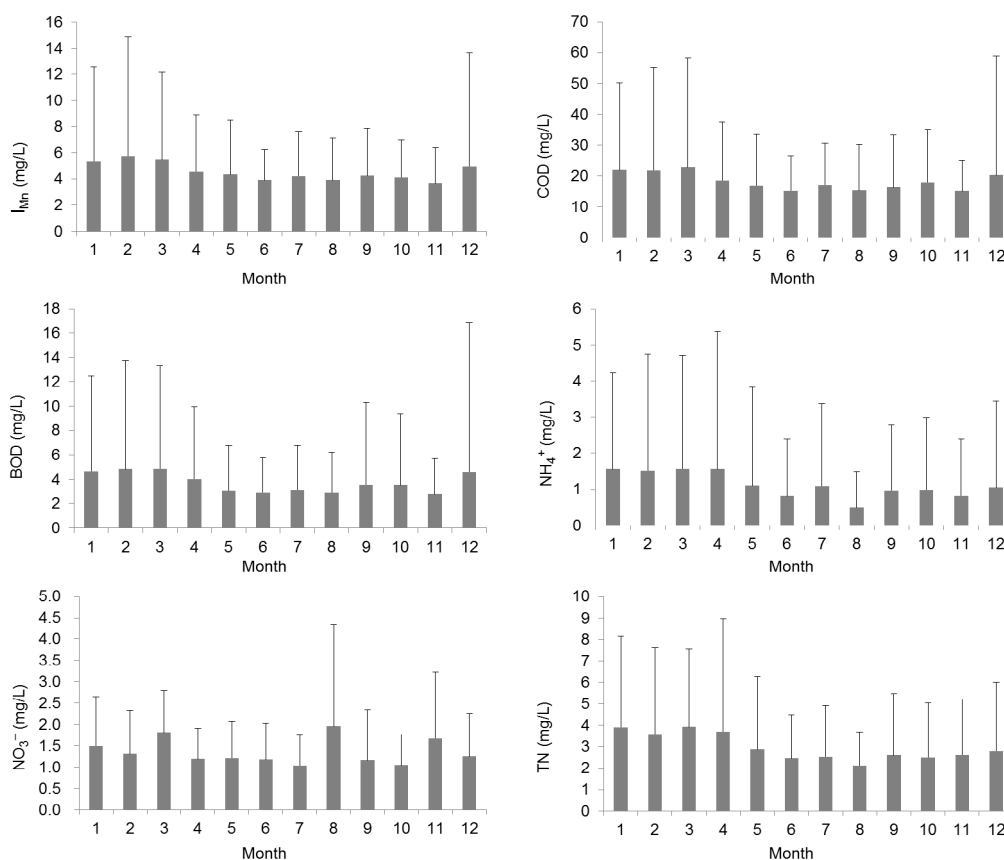

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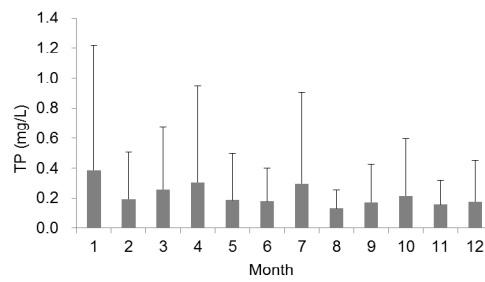
Figure 5. Seasonal dynamics of water nutrients (mean ± SD) in 27 subtropical rivers, China.
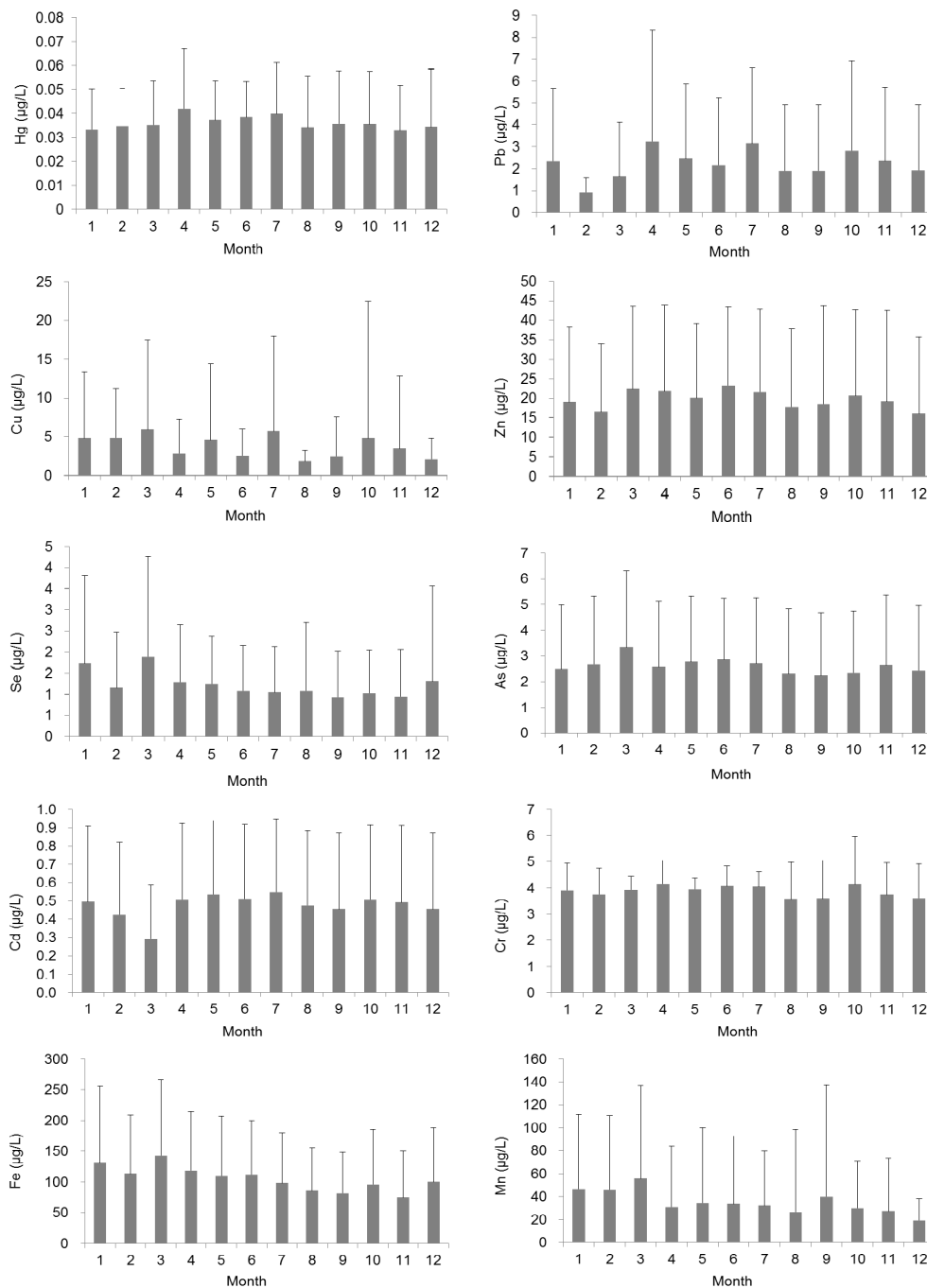

Figure 6. Seasonal dynamics of water heavy metals (mean ± SD) in 27 subtropical rivers, China.

3.4. Identification of Possible Pollution Sources

The PCA indicated that four principal components (PC) explained 80.87% of the total variance (Table 3). The PC1 accounted for 36.35% of the total variance and had strong positive loadings on I_{Mn}, COD, BOD_5, NH_4^+, TN, and Mn. The Pearson correlation analysis showed a positive relationship between nutrient variables (Table 4). Therefore, multiple nutrients might be discharged from the same pollution sources. The PC2, explaining about 18.61% of the total variance, had strong positive loadings on two metals (Hg and Cd) and a negative loading on NO_3^- (Table 3). The two heavy metals might come mainly from industrial processes (e.g., manufacture of electronic devices) in this region. The PC3 (14.13% of the total variance) had strong positive loadings on Zn and Fe, representing the metal pollution from mining and smelting activities. The PC4 (11.77% of the total variance) were most dependent upon Pb, Cu, and TP, and these elements likely originated from rock weathering and soil erosion (Table 3).

Table 3. Rotated component loadings of the first four principal components based on water nutrients and heavy metals.

Water Quality Parameters	Component			
	PC1	**PC2**	**PC3**	**PC4**
I_{Mn}	0.96	0.06	0.09	0.09
COD	0.97	0.12	0.12	0.06
BOD_5	0.96	0.08	0.08	0.02
NH_4^+	0.88	−0.13	−0.06	0.33
NO_3^-	0.16	−0.80	−0.05	0.02
TN	0.83	−0.35	−0.06	0.29
TP	0.56	−0.18	−0.08	0.69
Hg	0.26	0.66	0.16	0.01
Pb	−0.03	0.45	0.44	0.72
Cu	0.18	0.19	−0.25	0.77
Zn	0.06	0.23	0.86	0.00
Se	0.50	−0.04	−0.40	−0.21
As	0.38	0.41	−0.59	−0.22
Cd	−0.08	0.78	−0.03	0.34
Cr	0.03	0.04	0.21	0.14
Fe	0.34	−0.11	0.79	−0.36
Mn	0.79	−0.05	−0.03	−0.18
Eigenvalues	6.18	3.16	2.40	2.00
Percentage of variance	36.35	18.61	14.13	11.77
Cumulative percentage of variance	36.35	54.97	69.10	80.87

Table 4. Matrix of Pearson correlation coefficients for water nutrient and heavy metal parameters.

Water Quality Parameters	I_{Mn}	COD	BOD$_5$	NH$_4^+$	NO$_3^-$	TN	TP	Hg	Pb	Cu	Zn	Se	As	Cd	Cr	Fe	Mn
I_{Mn}	1																
COD	0.98 **	1															
BOD$_5$	0.97 **	0.99 **	1														
NH$_4^+$	0.86 **	0.84 **	0.85 **	1													
NO$_3^-$	0.07	0.05	0.09	0.27	1												
TN	0.77 **	0.75 **	0.75 **	0.94 **	0.48 **	1											
TP	0.58 **	0.52 **	0.45 *	0.69 **	0.16	0.69 **	1										
Hg	0.30	0.31	0.28	0.22	−0.26	0.10	−0.03	1									
Pb	0.09	0.13	0.08	0.11	−0.36	0.00	0.34	0.28	1								
Cu	0.25	0.22	0.18	0.32	−0.14	0.23	0.57 **	0.07	0.52 **	1							
Zn	0.10	0.15	0.12	−0.06	−0.26	−0.12	−0.07	0.18	0.51 **	−0.03	1						
Se	0.30	0.34	0.38	0.51 **	0.38	0.58 **	0.12	0.31	−0.33	−0.12	−0.29	1					
As	0.24	0.30	0.32	0.25	−0.03	0.21	−0.05	0.40 *	−0.18	0.20	−0.29	0.75 **	1				
Cd	0.00	0.04	0.02	−0.03	−0.56 *	−0.20	0.10	0.47 *	0.58 **	0.19	0.02	−0.07	0.17	1			
Cr	0.08	0.07	−0.03	−0.18	−0.32	−0.20	0.37	−0.36	0.24	0.20	0.34	−0.52 **	−0.31	0.00	1		
Fe	0.36	0.39 *	0.34	0.09	0.08	0.14	−0.04	0.09	0.03	−0.38	0.65 **	−0.12	−0.29	−0.24	0.27	1	
Mn	0.67 **	0.69 **	0.71 **	0.72 **	0.30	0.74 **	0.25	0.35	−0.18	−0.07	0.02	0.73 **	0.48 **	−0.14	−0.36	0.22	1

Notes: * $p < 0.05$; ** $p < 0.01$.

4. Discussion

4.1. Spatial and Seasonal Pattern of Water Quality in Subtropical Rivers

Spatial pattern analysis indicated that the highest values of I_{Mn}, COD, BOD_5, and NH_4^+ were all found in Lianjiang River (Figure 2). The Lianjiang River, originating in the Wufengshan Mountains, had a catchment area of approximately 1353 km^2 and a length of 71.1 km [34]. The river received large amounts of domestic sewage, industrial effluent and agricultural runoff from Jieyang City and Shantou City, which were the main industrial cities of Guangdong province. The Lianjiang River Basin had a GDP of 132.16 billion Chinese Yuan and a population of more than 4.3 million inhabitants in 2013. It was estimated that approximately 8.597×10^5 tons of domestic sewage and 2.025×10^5 tons of industrial wastewaters were produced per day in the Lianjiang River basin [34]. Unfortunately, nearly 83.2% of the domestic wastewaters in urban and rural settlements were not treated before discharge into the surrounding environments. The industrial wastewaters from 289 heavy polluting enterprises (most were textile and dyeing enterprises) were not fully treated because the illegal discharge of wastewaters was common in small enterprises. In addition, there were more than 70 large livestock and poultry farms in this basin, which produced large amounts of animal wastes and contributed significantly to the nutrient pollution of river water.

Our study found that the values of COD and BOD_5 in the dry season (from October to the next March) were significantly higher than those in the wet season (from April to September) in rivers draining into the South China Sea (Table 2). Many previous studies reported a similar observation in other subtropical regions. For instance, Li et al. (2009) demonstrated that dissolved N and P levels in river waters were relatively higher in the dry season than in the wet season in the upper Han River basin, China [11]. Moreover, Wang et al. (2010) indicated that the wet season had higher concentrations of nutrients and heavy metals than the dry season in water bodies in the Grand Canal of China [35]. These findings are probably partly due to high river flows and the resultant dilution effect in the wet season [2]. Another possible reason is that aquatic macrophytes growing in riparian wetlands and shallow water bodies can absorb and accumulate large quantities of contaminants in the wet season [35]. However, several studies did not match our above findings [36,37]. Hong et al. (2008) showed that the water TN and TP concentrations in the Xingfengjiang Reservoir basin in the dry season were not significantly different from those in the wet season [37]. The inconsistent results may be mainly attributed to the difference among catchments in terms of the land use composition and agricultural types, which strongly affect the outputs of nutrients and heavy metals. It has been reported that surface runoff in agricultural watersheds can contribute significant amounts of non-point source pollution to the receiving water bodies in the wet season [35].

4.2. Possible Source Identification of Pollutants in Subtropical Rivers

Pollutants including nutrients and heavy metals in river waters might originate from a number of natural and anthropogenic sources in terrestrial habitats [3,9]. The present study found that nutrients in rivers draining into the South China Sea might mainly come from domestic, industrial, and agricultural wastewaters. Many studies indicated that high N and P concentrations in aquatic ecosystems were generally related to high population density and intensive agricultural activities in catchments [38–42]. The percentage of cropland in Guangdong Province was approximately 18%, and most of the croplands were planted with rice, sugarcane, and vegetables [43]. With intensive agricultural development, excessive utilization of chemical fertilizers for enhancing crop productivity became a major environmental problem and resulted in water quality degradation and eutrophication in many rivers in Guangdong Province [27]. Fortunately, the non-point source pollution has attracted growing attention in recent years. A number of wastewater treatment technologies such as constructed wetlands, sand filters, and detention ponds have been widely used to remove pollutants from wastewaters in Guangdong Province [44].

Our study indicated that the sources of heavy metals in rivers draining into the South China Sea were varied. Although the mean concentrations of all measured heavy metals were relatively low, the maximum value of Fe and Mn exceeded the limit values for centralized drinking water sources in China (Table 1). We found that Fe and Zn might possibly come from mining and smelting activities. In general, mining and smelting were the main anthropogenic sources of Fe and Zn contamination in river water [20]. There were numerous mining and smelting factories in Guangdong Province, especially in the northern part of the province where many rivers and streams (e.g., the Pearl River) originated [20]. Two highly toxic metals (Hg and Cd) might mainly come from various industrial sources including electronic factories, industrial boilers, power plants and cement plants [45]. Although Zinc smelting was recognized as one of the most important sources of Hg emission [45], it may not be the main source of Hg in Guangdong Province because our data showed a non-significant relationship between Hg and Zn concentrations in river waters.

5. Conclusions

This study investigated the water nutrient and heavy metal pollution in 27 subtropical rivers draining into the South China Sea and found that the averages of most water quality parameters were lower than the corresponding values of the grade III water quality standard of China. Spatial pattern and cluster analyses revealed that the Lianjiang River was the most polluted, with the highest levels of I_{Mn}, COD, BOD_5, NH_4^+, Hg, Fe, and Mn. The river water quality showed a significant difference in seasonal variations of COD, BOD_5 and Hg during the dry and wet seasons. PCA demonstrated that nutrients might originate from domestic, industrial and agricultural wastewaters, while heavy metals likely came from industrial activities and natural processes. Although the local governments have paid great attention to the water quality improvement in rivers draining to the South China Sea, our findings suggest that more efforts should be made to control the nutrients exported from catchments in the future. In addition, further studies using isotope techniques are needed to more precisely determine the sources of nutrients and heavy metals in these rivers.

Author Contributions: Amei Deng and Wenzhi Liu designed the study; Changdong Ye collected the data; Amei Deng and Changdong Ye analyzed the data; Amei Deng and Wen Liu wrote the article.

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

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