Nutrient and Trace Metal Issues in the Pearl River Delta, China

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Abstract The Pearl River Delta (PRD) has undergone rapid urban growth and industrial development during the past four decades, and human activities have become one of the most important factors affecting the environment in the region. Therefore, there is an urgent need to examine the influence of urbanization on surface water and groundwater systems. Based on data collection and analyses of industry, agriculture, environmental protection efforts, natural conditions, and population statistics in 2000, 2005, and 2010, we assessed the nitrogen (N) and phosphorus (P) budgets and their regional differences in the PRD between the three time periods. The N and P input and output varied greatly during 2000–2010, whereas the N and P surplus increased continuously. In addition, intense human activities induced severe trace metal pollution in the Shima River close to an important water supply source. Zinc and copper concentrations markedly exceeded the national water quality standards (Class I) in the dry season. Meanwhile, various pollution sources significantly contributed to metal accumulation in riverine sediments, leading to a slight enrichment in lead, manganese, and iron, and moderate-to-heavy enrichment of chromium, nickel, copper, zinc, and cadmium. Hierarchical cluster analysis indicates that sediment pollution caused by trace metals was mainly associated with industrial and agricultural activities.

Keywords Pearl River Delta · Environmental mediums · Nutrients budget
Trace metals pollution · Water safety

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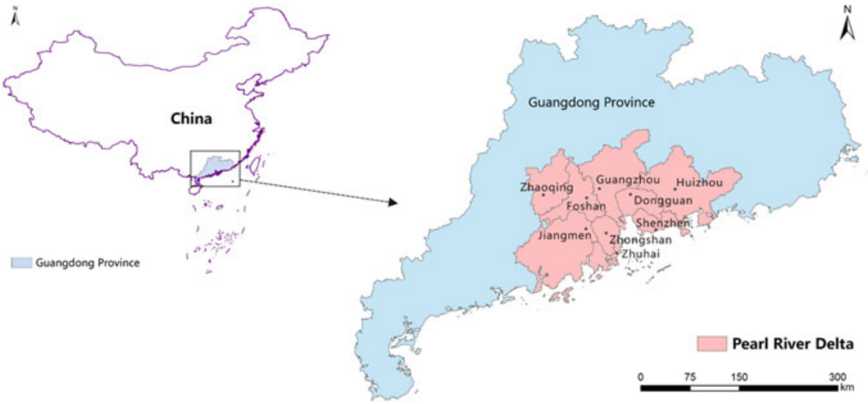


Fig. 1 Location of the Pearl River Delta

1 Introduction

The Pearl River Delta (PRD) is one of the highly developed areas in China. Geographically, it includes nine cities, i.e., Guangzhou, Shenzhen, Zhuhai, Foshan, Huizhou, Zhaoqing, Jiangmen, Zhongshan, and Dongguan, with a total area of 41,700 km^2 (Fig. 1). Since the beginning of China's economic reform in 1978, this region has undergone rapid industrialization and urbanization, making it one of the largest manufacturing centers in China. During 1978–2007, the gross domestic product (GDP) in the PRD region increased at an average annual rate of 21.2%, accounting for approximately 10.2% of the total national GDP in 2006 (Huang et al. 2012). However, rapid socioeconomic development comes at the cost of the environment. According to Chen et al. (2006a, b), more than 3×10^9 tons of industrial and domestic wastewater were annually discharged into surface water systems, which resulted in increasing levels of trace metals and nutrients, ultimately leading to severe environmental issues such as pollution and eutrophication of surface water bodies.

Nitrogen (N) and phosphorus (P) play crucial roles in many biogeochemical processes and functions as important controlling factors in terrestrial and aquatic ecosystems. The N and P cycles are the two major material cycles of the earth's bio-, atmo-, hydro-, and geo-spheres. In recent centuries, the development of human civilization, accompanied by rapid urbanization, explosive population growth, and industrial and agricultural revolutions, tremendously increased nutrient input into the environment, altering N and P cycles. While contributing to the growth of agricultural and industrial production, excessive N and P accumulate on land or are discharged into water or atmosphere, exacerbating environmental problems including the greenhouse effect, eutrophication, and acid rain, with visible effects on land and sea, particularly in coastal areas. Since about 60% of the human populations live within 100 km from coasts, eutrophication in coastal waters can cast an immediate impact on humans, making it a global concern (Valiela et al. 1992; Jonge et al. 2002).

Trace metal pollution has received increasing interest due to its unique physicochemical properties (e.g., persistence, non-degradability, toxicity, and bioaccumulation) (Li et al. 2013), can have adverse impacts on aquatic organisms through bioaccumulation and biomagnification, thus causing health problems after entering the food chain (Varol and Şen 2012). Furthermore, water pollution caused by heavy metals directly threatens human health via water consumption. Thus, heavy metals pollution is arousing growing public concerns worldwide.

In general, the PRD area suffered from complex sources of pollution (e.g. nutrients and heavy metals, organic compounds). Understanding the distribution, magnitude, potential sources and environmental behaviors of major pollutants in the different mediums is important for implementing pollution prevention and control measures. However, little research regarding the nutrients and metals pollution has been done in the highly urbanized watersheds of the PRD region. Consequently, the aims of our study were: (1) to estimate nutrients budgets in the whole PRD area, (2) to select Tangjiawan town as one of the study areas in Zhuhai city to investigate spatial and temporal characteristics of major nutrients (nitrogen and phosphorous) in different water bodies, (3) to assess trace metals pollution in the river and sediments from the Shima River, a highly urbanized watershed close to an important water supply source in Dongguan city, and (4) to reveal the impacts of human activities on the environmental behaviors of nutrients and trace metals in water bodies, and to preliminarily identify their potential sources.

2 Case Study: Nitrogen and Phosphorus Budgets in the PRD Area

The N and P budgets within a given region will need to be quantitatively evaluated before they can be effectively understood and managed. In the past 30 years, the PRD has experienced economic growth, urbanization, and human activities on an unprecedented scale, and the resulting changes and regional variations in N and P budgets and nutrient output in water deserve intensive studies. This section examines relevant data for the years of 2000, 2005, and 2010, and explores the N and P budgets of the PRD including their histories, regional variations, and potential impacts. All data related to N and P budget calculation were collected from the *Statistical Yearbook of Guangdong Province* for each year published by the provincial Bureau of Statistics, including land cover area, population, agriculture, industries, and environmental protection information for the nine cities of the PRD.

2.1 Nitrogen Budget Estimates and Regional Variation Analysis

Input, output, and surplus are three components that are necessary to estimate a regional N budget. The parameters and computation methods below are partially based on several existing studies (Galloway et al. 1996; Zhu 1997; Xing and Yan 1999; Xing and Zhu 2000, 2002; Galloway 2005; Nancy and Carly 2005; Liu et al. 2006; Deng et al. 2007; Russell et al. 2008; Chen and Jia 2009).

2.1.1 Nitrogen Input: General Features and Regional Variation

The N input of the nine PRD cities was calculated for 2000, 2005, and 2010 based on their statistics (Table 1). The total N input of the PRD did not vary much during the three periods, ranging from 84.71 × 10^4 to 91.16 × 10^4 t, and it was slightly lower in 2010 than in 2000. Each N source generally had a similar contribution rate in the three periods and across the regions, showing the descending order of fertilizer, human and livestock excreta, wet deposition, wastewater NH_3-N, farmland symbiotic fixation, crop residue, and farmland non-symbiotic fixation. This is consistent with the estimates by other studies on the Beijiang River Basin (Chen and Jia 2009), the Yangtze River Delta (Deng et al. 2007), the three major drainage basins of China (i.e., the Yangtze, Yellow, and Pearl Rivers) (Xing and Zhu 2002), and the North Atlantic Region (Howarth et al. 1996), where fertilizer, excreta, and wet deposition ranked as the top three N input factors. The results can be closely related to the current agricultural activities and population distributions in China, where economic prosperity and robust industrial activities in the three major catchments have led to the massive use of chemical fertilizers, making them the largest N input sources. As the economic boom attracts more people into the PRD, their demands for meats, eggs, and dairy products have contributed to N input through excreta. Wet deposition is another major N input, which can be likely attributed to NO_X compounds discharged into the atmosphere by fossil fuel combustion during vehicle transportation; the compounds are deposited back onto land and into water bodies via the region's ample precipitation.

The relative contributions of nine cities to the N input in the three periods were similar (Table 1), following the descending order of Zhaoqing, Guangzhou, Jiangmen, Huizhou, Foshan, Dongguan, Shenzhen, Zhongshan, and Zhuhai. Figure 2 compares the N loads in each city, providing an overview of the N input intensity, where the dotted line represents the PRD average, and the N load is the total N input per unit land area. The N load ranking of each city differs somewhat from its N input ranking. The N load values range from 114.96 to –303.73 kg/hm^2 a. Shenzhen always had the highest N load, which increased over the decade-long study period. Rapid population and industrial growth in Shenzhen were reflected by the fastest-increasing N sources, excreta and wastewater, which rose from 2.62 × 10^4 and 0.99 × 10^4 t in 2000 to 3.61 × 10^4 and 1.54 × 10^4 t in 2010, respectively. Conversely, the N load of Zhuhai fell from 246.37 kg/hm^2 a in 2000 to 131.67 kg/hm^2 a in 2010. The largest

Table 1 Nitrogen inputs in the Pearl River Delta by city and time period (in 10^4 t)

City (Region)	Year	Fertilizer	Farmland symbiotic fixation	Farmland Non-S fixation	Human and livestock excreta	Wet deposition	Waste water NH_3-N	Crop residue	Total input
Guangzhou	2000	6.18	0.26	0.51	4.44	2.60	2.20	0.30	16.50
	2005	5.34	0.11	0.55	4.07	2.87	1.78	0.15	14.86
	2010	5.78	0.09	0.53	5.55	3.10	1.84	0.11	16.99
Shenzhen	2000	0.22	0.00	0.02	2.62	0.98	0.99	0.00	4.82
	2005	0.19	0.00	0.01	2.92	0.83	1.13	0.00	5.08
	2010	0.14	0.00	0.01	3.61	0.63	1.54	0.00	5.93
Zhuhai	2000	2.31	0.01	0.11	0.57	0.82	0.23	0.03	4.07
	2005	0.46	0.00	0.06	0.63	0.72	0.20	0.02	2.10
	2010	0.39	0.00	0.08	0.80	0.59	0.30	0.01	2.18
Foshan	2000	3.12	0.05	0.22	2.61	1.12	0.60	0.14	7.86
	2005	2.67	0.03	0.19	2.76	1.28	0.68	0.04	7.64
	2010	2.39	0.02	0.20	3.34	1.53	1.20	0.02	8.71
Huizhou	2000	5.49	0.39	0.30	2.84	5.20	0.22	0.33	14.76
	2005	5.22	0.38	0.37	2.94	3.84	0.21	0.20	13.18
	2010	5.34	0.26	0.34	3.01	4.03	0.46	0.16	13.58
Dongguan	2000	1.32	0.01	0.09	2.95	0.99	0.77	0.07	6.21
	2005	0.60	0.00	0.15	2.87	0.90	1.07	0.00	5.60
	2010	0.54	0.00	0.12	2.94	0.87	1.12	0.00	5.59

(continued)

Table 1 (continued)

City (Region)	Year	Fertilizer	Farmland symbiotic fixation	Farmland Non-S fixation	Human and livestock excreta	Wet deposition	Waste water NH_3-N	Crop residue	Total input
Zhongshan	2000	1.48	0.01	0.11	0.96	0.72	0.20	0.08	3.55
	2005	1.17	0.00	0.08	1.03	0.64	0.27	0.04	3.23
	2010	1.00	0.00	0.10	1.28	0.68	0.52	0.01	3.60
Jiangmen	2000	7.11	0.29	0.32	2.80	3.43	0.46	0.44	14.84
	2005	6.03	0.24	0.53	2.85	3.36	0.37	0.28	13.66
	2010	6.21	0.16	0.42	2.92	4.33	0.46	0.26	14.77
Zhaoqing	2000	7.35	0.30	0.27	4.26	4.19	0.23	0.45	17.04
	2005	7.61	0.33	0.53	4.89	3.96	0.22	0.37	17.91
	2010	7.44	0.30	0.40	4.17	4.84	0.34	0.33	17.82
In total	2000	34.58	1.32	1.95	24.04	21.54	5.90	1.82	91.16
	2005	29.30	1.09	2.47	24.96	19.85	5.94	1.08	84.71
	2010	29.22	0.84	2.21	27.62	20.49	7.78	0.90	89.06

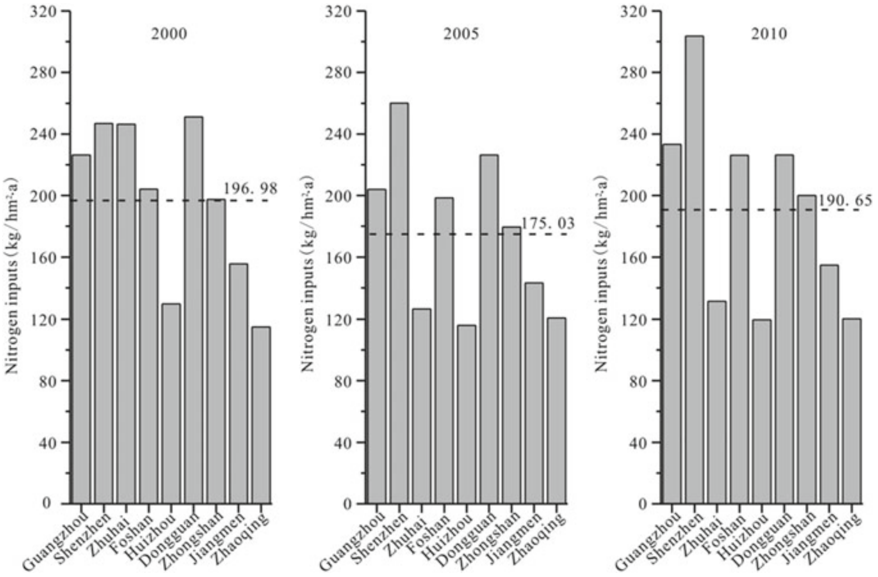


Fig. 2 Comparison of nitrogen (N) inputs per unit land area in the Pearl River Delta (PRD) by city and period

change occurred in fertilizer N, which decreased from 2.31 × 10^4 t in 2000 to 0.39 × 10^4 t in 2010. This can be explained by the increase in urbanization and reduction of farmland area from 12.68 × 10^4 hm^2 in 2000 to 1.74 × 10^4 hm^2 in 2010. The N loads of the other cities did not vary much. Overall, the PRD had a higher average N load than the national mean (~64 kg/hm^2 a) and the Pearl River drainage basin (~104.44 kg/hm^2 a) (Xing and Zhu 2002), but was lower than that of the Yangtze River Delta (~291 kg/hm^2 a) (Deng et al. 2007).

2.1.2 Terrestrial Nitrogen Flux

The terrestrial N flux (TNF) is an important indicator of the environmental impact of N in a region (Howarth et al. 1996), and is defined as the sum of fertilizer N and excreta N per unit land area within a year. The TNF values in the PRD were computed and compared (Fig. 3).

TNF values tend to exhibit high regional variation throughout the world due to differences in population density, human activities, and industrial technologies. Around the North Atlantic, the mean TNFs have been reported as 15–13 kg/hm^2 a in the North Sea and northwestern coasts of Europe, 11 kg/hm^2 a along the northeastern coast of the United States, and 8 kg/hm^2 a in the northern riverine regions of Canada (Howarth et al. 1996). In China, the mean TNF (Deng et al. 2007) increased from 1950s about 6 kg/hm^2 a to nearly 45 kg/hm^2 a in 1999. The TNF values for 2000,

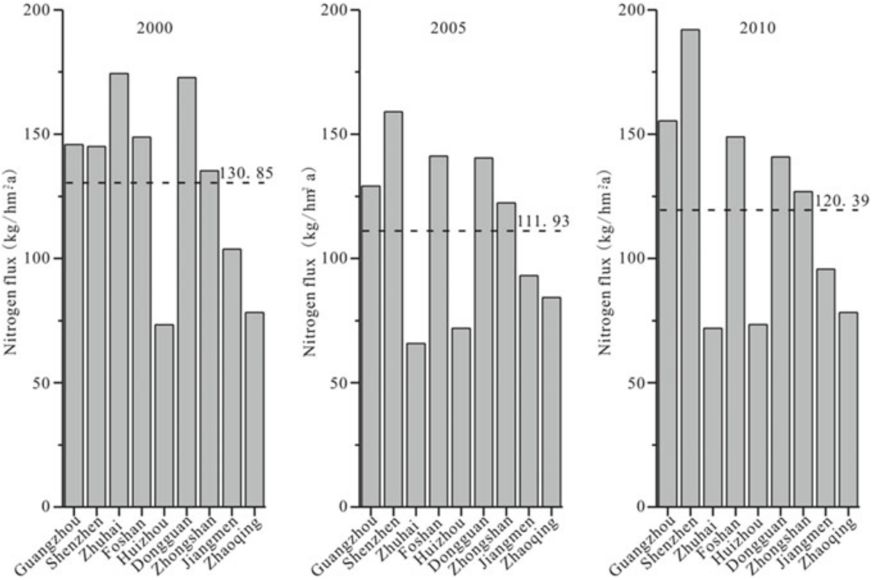


Fig. 3 Comparison of terrestrial N fluxes in the PRD by city and period

2005, and 2010 were 130.85, 111.93, and 120.39 kg/hm^2 a, respectively, exceeding the previous values but were still below that of the Yangtze River Delta (224 kg/hm^2 a). The city-specific TNF values were between 73.38 and 192.06 kg/hm^2 a, and Shenzhen, Guangzhou, Foshan, Dongguan, and Zhongshan had values higher than the average in all three periods, possibly due to their stronger economic growth and higher population densities. The TNF of Zhuhai decreased from 174.45 kg/hm^2 a in 2000 to 71.91 kg/hm^2 a in 2010. The other cities, Huizhou, Jiangmen, and Zhaoqing, had values significantly lower than the average. Based on these results, the five higher-than-average cities are at a greater risk due to N-related environmental issues.

2.1.3 Nitrogen Output: General Features and Regional Variation

Table 2 presents the estimated N outputs of the nine PRD cities in 2000, 2005, and 2010. The total N output in the PRD ranged from 56.82 × 10^4 to 67.38 × 10^4 t for the three periods. The major contributions were from water bodies and denitrification, followed by crop harvesting and vaporization. The N output via crop harvesting significantly declined over the study period (Table 2), from 14.50 × 10^4 t in 2000 to 7.18 × 10^4 t in 2010, with a decrease of over 50%. This provides additional evidence of the effects of the decrease in farmland area and increase in urbanization in the PRD. According to the Statistical Yearbook of Guangdong Province (2000 and 2010), the total cropland in the PRD region was 189.47 × 10^4 hm^2 in 2000 and 131.21 × 10^4 hm^2 in 2010, showing a decrease by about one-third over a period of 10 years. In

Table 2 Nitrogen outputs in the Pearl River Delta by city and time period (in10^4 t)

City (Region)	Year	Vaporization	Harvested crops	Export by water bodies	Denitrification	Total output
Guangzhou	2000	1.55	2.38	4.82	3.30	12.06
	2005	1.39	1.17	4.41	2.97	9.95
	2010	1.73	0.88	5.48	3.40	11.49
Shenzhen	2000	0.55	0.00	2.04	0.96	3.56
	2005	0.61	0.00	2.38	1.02	4.01
	2010	0.74	0.00	2.96	1.19	4.88
Zhuhai	2000	0.35	0.22	1.08	0.81	2.47
	2005	0.19	0.12	0.55	0.42	1.27
	2010	0.20	0.08	0.58	0.44	1.30
Foshan	2000	1.12	1.08	2.53	1.57	6.30
	2005	0.97	0.28	2.49	1.53	5.28
	2010	1.09	0.18	2.80	1.74	5.82
Huizhou	2000	1.71	2.62	2.77	2.95	10.06
	2005	1.29	1.65	2.85	2.64	8.43
	2010	1.54	1.27	3.07	2.72	8.60
Dongguan	2000	0.88	0.53	2.24	1.24	4.89
	2005	0.63	0.03	2.07	1.12	3.85
	2010	0.68	0.02	2.51	1.12	4.32
Zhongshan	2000	0.46	0.61	1.14	0.71	2.93
	2005	0.42	0.27	1.06	0.65	2.40
	2010	0.44	0.10	1.21	0.72	2.46
Jiangmen	2000	2.16	3.48	3.42	2.97	12.03
	2005	1.28	2.21	3.19	2.73	9.41
	2010	1.68	2.04	3.29	2.95	9.96
Zhaoqing	2000	2.50	3.57	3.32	3.41	12.80
	2005	1.85	2.93	3.57	3.58	11.93
	2010	2.10	2.62	3.54	3.56	11.83
In Total	2000	11.29	14.50	23.37	18.23	67.38
	2005	8.64	8.67	22.57	16.94	56.82
	2010	10.21	7.18	25.44	17.81	60.65

addition, there was an increasing trend in the export of N via water bodies, which was mainly attributed to artificially activated N and N in waste directly discharged into water, another sign of the increasing human impacts on the N cycle.

The contribution of each city to the N output was similar over the study period (Table 2), and the ranking showed the same decreasing trend as the N input: Zhaoqing, Guangzhou, Jiangmen, Huizhou, Foshan, Dongguan, Shenzhen, Zhongshan, and Zhuhai. In terms of the N output fluxes (total N output per unit land area) shown in Fig. 4, where the dotted lines represent the PRD average, Shenzhen had the highest

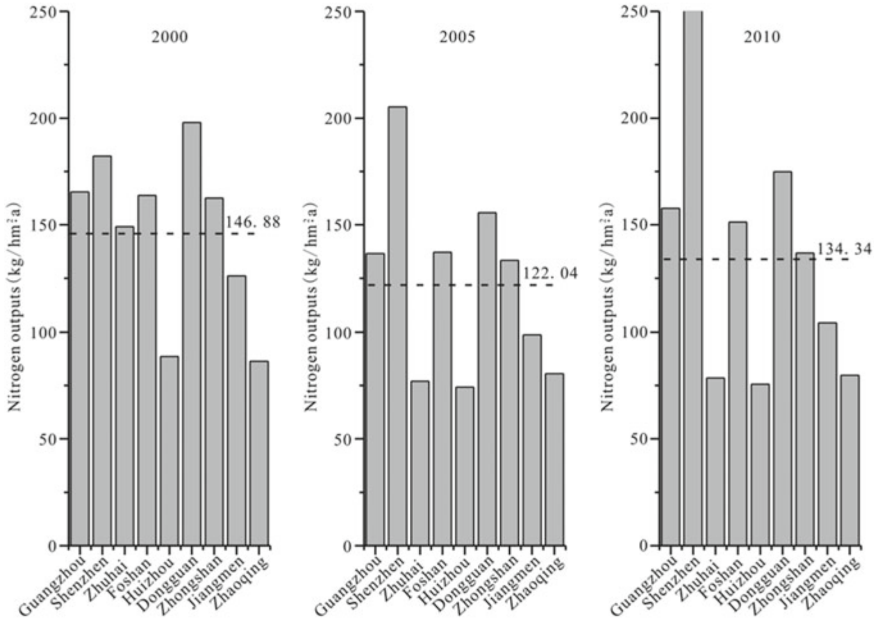


Fig. 4 Comparison of N outputs per unit land area in the Pearl PRD by city and period

values, followed by Dongguan, Guangzhou, Foshan, Zhongshan, Jiangmen, Zhuhai, Zhaoqing, and Huizhou. In particular, the N output flux of Shenzhen exhibited a rapidly increasing trend between 2000 and 2010.

2.1.4 Nitrogen Surplus

The N surplus (total N input minus total N output) in the PRD increased (Table 3) from 23.77×10^4 t in 2000 to 28.42×10^4 t in 2010, which was significantly higher than that of the neighboring Beijiang River Basin (~9.67×10^4 t/a) (Chen and Jia 2009), but substantially lower than that of the Yangtze River Delta ($99 \sim 128 \times 10^4$ t/a) (Deng et al. 2007). The N surplus per unit land area increased from 43.43 kg/hm^2 a in 2000 to 50.95 kg/hm^2 a in 2005 and 51.92 kg/hm^2 a in 2010. Zhaoqing had the highest total N surplus, followed by Guangzhou, Huizhou, Jiangmen, Foshan, Dongguan, Zhongshan, Shenzhen, and Zhuhai. However, Guangzhou had the highest surplus per unit land area, followed by Zhuhai, Shenzhen, Dongguan, Foshan, Zhongshan, Jiangmen, Huizhou, and Zhaoqing. Surplus N per unit land area, mostly held in soils, plants, and water bodies, has an important influence on any potential N-related pollution; therefore, Guangzhou, Zhuhai, Shenzhen, Dongguan, and Foshan are at greater risk of the effects of N-related pollution.

Table 3 Nitrogen budgets in the Pearl River Delta in the three time periods

Year	Input (10^4 t)	Output (10^4 t)	Surplus (10^4 t)	Surplus per unit land area (kg/hm^2 a)
2000	91.16	67.38	23.77	43.43
2005	84.71	56.82	27.89	50.95
2010	89.06	60.65	28.42	51.92

Table 4 Phosphorus budgets in the Pearl River Delta in the three time periods

Year	Input (t)	Output (t)	Surplus (t)	Surplus per unit land area (kg/hm^2 a)
2000	144506.38	52635.80	91870.58	16.79
2005	138771.14	45584.81	93186.34	17.03
2010	147317.40	39484.53	107832.88	19.70

2.2 *Phosphorus Budget Estimates*

Similar to N, input, output, and surplus are the three components of a regional P budget. The parameters and computation methods below are partially based on several existing studies (e.g., Xing and Yan 1999; Xing and Zhu 2002; Yang et al. 2006; Russell et al. 2008; Wang et al. 2009; Fan et al. 2010; Liu et al. 2011a, b).

2.2.1 Phosphorus Budget: General Features

The P input of the nine PRD cities was calculated for 2000, 2005, and 2010 based on the statistical data in Table 4. The total input was slightly lower in 2005 than in 2000 but slightly higher in 2010 than in 2000, with an increase of about 6% from 2005 to 2000. However, the total P output significantly declined over the study decade, decreasing by about 25% from 2000 to 2010. These changes considerably increased the P surplus of the PRD. Such an unbalance between P input and output is likely to lead to eutrophication of water bodies. Because both the total amount and per unit area amount of the P surplus increased, the PRD is under great threat of P pollution, and management of the P budget is an important task for local authorities.

2.2.2 Phosphorus Input and Its Regional Variation

The largest source of P input in all three periods was human and livestock excreta, accounting for more than 50% of the contribution in each year (Fig. 5). This was followed by fertilizer, with an average contribution of around 43%. The effects of atmospheric deposition and crop residue were small, contributing less than 5% of the total P input. These results are similar to those reported in other regions of

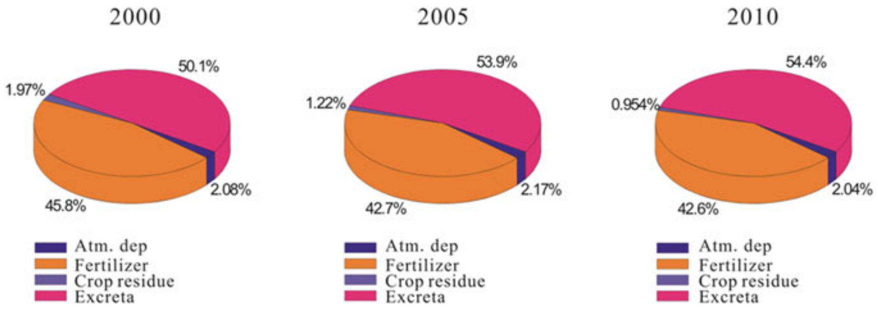


Fig. 5 Phosphorus (P) input sources in the PRD in the three studied periods

China (Wang et al. 2009; Liu et al. 2011a, b), where excreta and fertilizers are the most important P input sources. This can be related to the large population and large numbers of livestock required to meet the demand for meats, eggs, and dairy products. Fertilizer was another major source of P due to the high rate of fertilizer use in the region, which loses P via soil erosion. Another feature was the increase in excreta P, with 72,434.87 t, 74,834.97 t, and 80,074.78 t in 2000, 2005 and 2010, respectively. In contrast, crop residue P showed a declining trend of 2,850.72 t, 1,693.14 t, and 1,405.76 t in the three respective periods, accounting for a 50% decrease over the decade. The former was related to the booming population, particularly migrant workers from other regions, and the latter to a reduction in farmland area due to urbanization.

The P input differed significantly across the cities, as shown in Fig. 6, where the dotted lines indicate the PRD average. Zhaoqing had the highest P inputs, followed by Guangzhou, Jiangmen, Huizhou, Foshan, Dongguan, Shenzhen, Zhongshan, and Zhuhai. This was due to the larger area of farmland in Zhaoqing, Jiangmen, and Huizhou, which required more fertilizer, the most important source of their P inputs. Foshan, Dongguan, Shenzhen, Zhongshan, and Zhuhai had smaller areas of farmland, and therefore, excreta became the most important P source. Guangzhou had both a large population and a large farmland area, which explains why the two sources were relatively comparable.

In terms of the P input (Fig. 6), Shenzhen, Dongguan, and Zhuhai showed a significant variation among years, which was not the case for the other cities. The P input per unit area in Shenzhen increased from 37.68 kg/hm^2 a in 2000 to 48.86 kg/hm^2 a in 2010. Excreta had the highest contribution rate, which also increased over the study period. Specifically, the total P input in Shenzhen was 6,837.24, 7,417.0, and 9,130.89 t in 2000, 2005, and 2010, showing an increase of approximately 33% over the decade. The P input per unit area in Dongguan and Zhuhai decreased in 2010 compared to those in 2000, predominantly driven by the decrease in fertilizer P use. Notably, fertilizer P in Zhuhai decreased from 4,430.55 t in 2000 to 843.08 t in 2010,

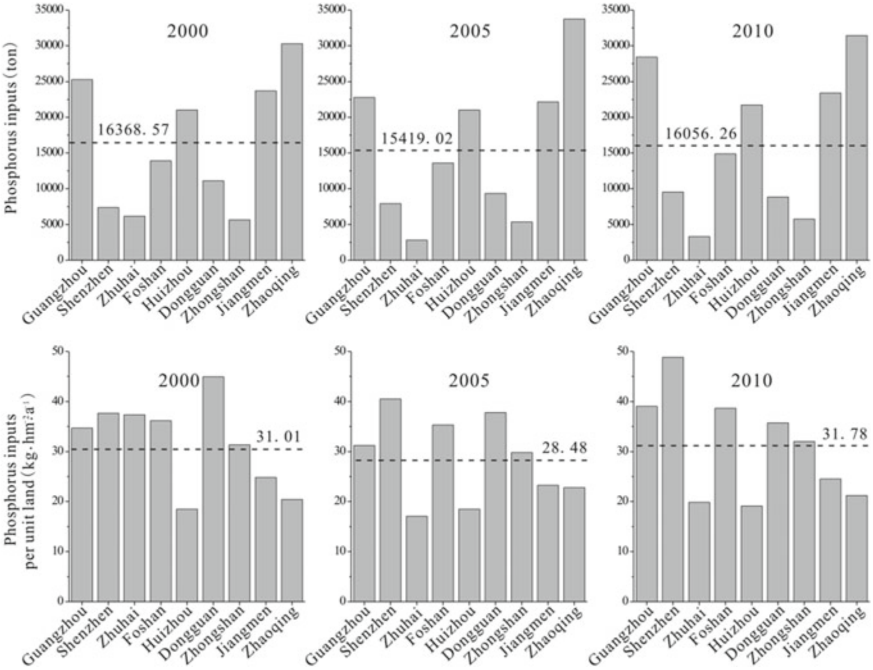


Fig. 6 Comparison of total P inputs and inputs per unit land area in the PRD

an approximately 80% decrease over the 10-year study period, in accordance with its urbanization and reduction in farmland area.

2.2.3 Phosphorus Output and Its Regional Variation

The most frequent destination for P output in the PRD was crop harvests and P stored in livestock, contributing to over 60% and 23% of the total P output respectively (Fig. 7). Soil erosion had a smaller effect (~11%), and export via runoff had the lowest contribution (~2%), which are similar to previous reports s (e.g., Wang et al. 2009; Liu et al. 2011a, b). Since PRD is a flood plain with good vegetation coverage and effective soil retention measures in place, soil erosion should not be a major problem.

Figure 8 shows the P output in the three periods, where the dotted lines represent the average values. The average P output decreased from 5,848.42 t in 2000 to 4,387.16 t in 2010. Crop harvests made the greatest contribution, decreasing from 36,150.91 t in 2000 to 24,753.81 t in 2010, indicating a reduction in farmland for crop production. The next greatest contribution was P stored in livestock, which

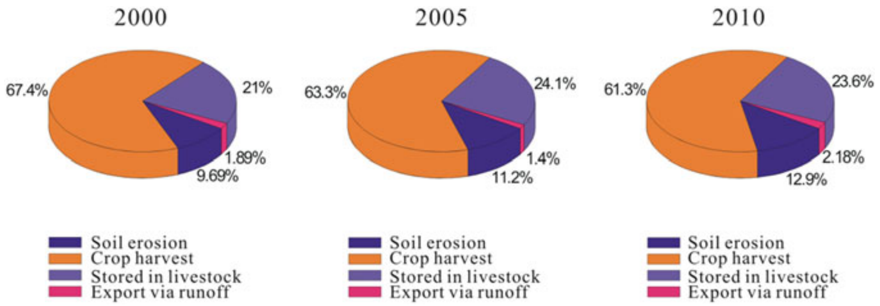


Fig. 7 Phosphorus output destinations in the PRD in the three studied periods

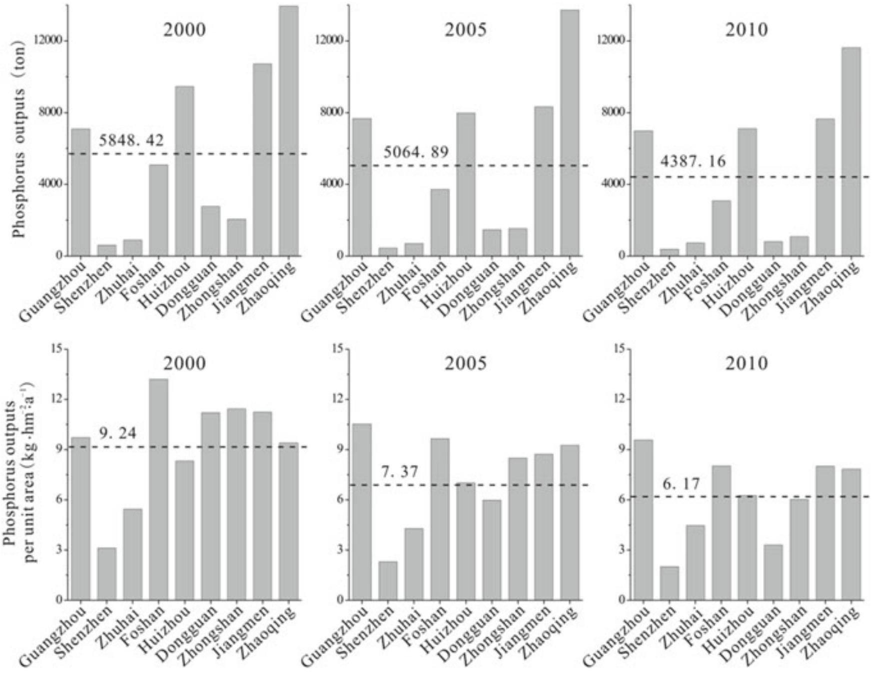


Fig. 8 Comparisons of total P outputs and outputs per unit land area in the PRD

decreased by about 1,800 t from 2000 to 2010. The region with the largest P output was Zhaoqing, followed by Jiangmen, Huizhou, Guangzhou, Foshan, Zhongshan, Dongguan, Zhuhai, and Shenzhen, with farmland area, livestock, and soil retention as the most important determining factors. In particular, Zhaoqing, Jiangmen, and Huizhou displayed considerable P outputs via crop harvests. Although the P output per unit area decreased significantly in the PRD, the values were still relatively high in Foshan, Guangzhou, Jiangmen, Zhaoqing, and Zhongshan.

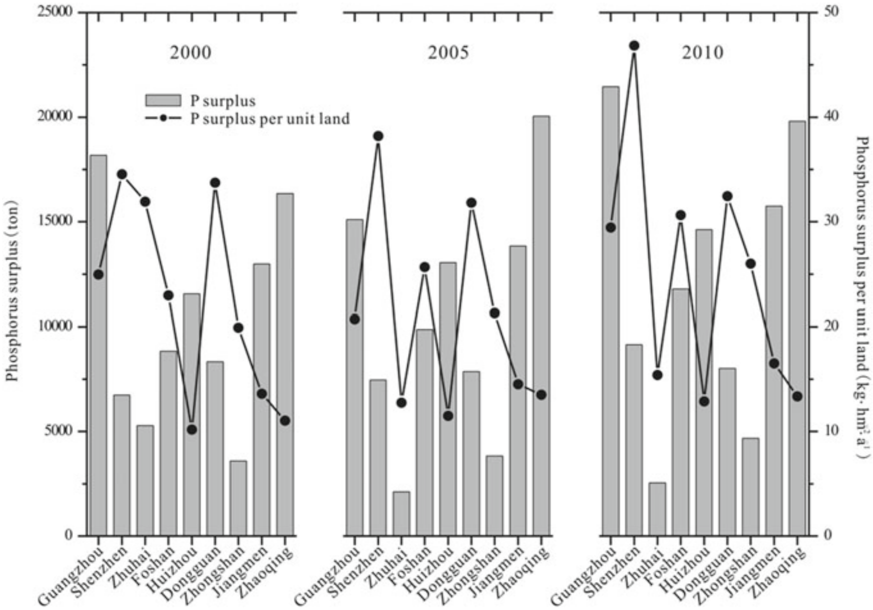


Fig. 9 Comparison of the total P surplus and surplus per unit land area in the PRD

2.2.4 Phosphorus Surplus

The P surplus results (Table 4 and Fig. 9) showed a gradual increase in the total P surplus, from 91,870.58 t in 2000 to 107,832.88 t in 2010. The P surplus per unit area also increased, and was 16.79, 17.03, and 19.70 kg/hm^2 a in 2000, 2005, and 2010, respectively. The P surplus per unit area was relatively low, which was even lower than the national average (Cao et al. 2009). A significant regional variation was observed among cities, with Zhaoqing showing the highest total surplus, followed by Guangzhou, Jiangmen, Huizhou, Foshan, Dongguan, Shenzhen, Zhongshan, and Zhuhai. In terms of the average surplus per unit area over the three periods, Shenzhen had the highest surplus, followed by Dongguan, Foshan, Guangzhou, Zhongshan, Zhuhai, Jiangmen, Zhaoqing, and Huizhou. In particular, Shenzhen, Dongguan, Foshan, Guangzhou, and Zhongshan had a higher surplus per unit area compared to the PRD average, indicating a higher risk of P-related pollution.

3 Case Study: Nitrogen and Phosphorus Pollution in Groundwater of the Tangjiawan Town, Zhuhai

3.1 Study Area and Water Sampling

Zhuhai is a prefecture-level city located at the west bank of the Pearl River in southern Guangdong Province. It is separated from Shenzhen and Hong Kong to the east by the sea, and is connected to Macau to the south by land. Located at 21°43′–22°29′N and 113°03′–114°24′E, Zhuhai has a subtropical monsoon climate, with an average annual temperature of 22.4 °C, average annual precipitation of 2011 mm, and average annual evaporation of around 1,469 mm. It has two very different seasons, the rainy season (April–September) and the dry season (October–March). Surrounded by mountains and ocean, the region has diverse geographical and ecological environments, including 731 km of coastlines and good vegetation coverage with predominantly subtropical plant species.

Located in northern Zhuhai, Tangjiawan is a town with 130 km^2 in size and a total population of about 100,000. It is governed by 16 neighborhood committees. It includes five university campuses housing 15,000 students, including the Zhuhai Campus of Sun Yat-sen University (ZCSYSU) and that of Beijing Normal University. It is also the home to high-tech industrial parks, such as the Tsinghua (Zhuhai) Technology Park and National Software Base. In this study, water samples were collected in two areas, ZCSYSU and the Tangjiawan residential area (Fig. 10), which are located 1 km from each other and have similar hydrogeological settings but differ in terms of the intensity of human activities. ZCSYSU is a small catchment (3.4 km^2) facing the sea. It is enclosed by hills on the other three sides and experiences a relatively lower human impact. Here, we set up flow weirs A and B in the upper and lower ends of the fault gully in the upper segment of the catchment, and 14 observation wells along the stream outside the gully (Table 5), including 3 in the recharge area (R1–R3), 5 in the middle area (M1–M5), and 6 in the discharge area (D1–D6). The Tangjiawan residential area is located at the eastern side of Eling Mountain to the north of ZCSYSU, and also faces the sea. Other than several public facilities, the area largely contains residential houses and protected historical buildings. Public wells are found throughout the mountain slope alongside residential buildings, and the local groundwater has experienced varying degrees of human-induced pollution.

During the period from July 2009 to June 2010, water samples were collected once per month from flow weirs A and B (surface water), 14 observation wells in the campus (groundwater), and 7 public wells in the Tangjiawan residential area (groundwater), with some parameters measured in situ, including temperature, pH, electric conductivity, dissolved oxygen, and oxidation-reduction potential. In total, 24 surface water samples and 262 groundwater samples were obtained. From 2006 to 2007, 41 rainwater samples were collected at the campus as well. The samples were analyzed for cations and anions by the IRIS Advantage (HR) spectrometer (Thermo Jarrell Ash) and the DX-600 ion chromatographer (Dionex) respectively at

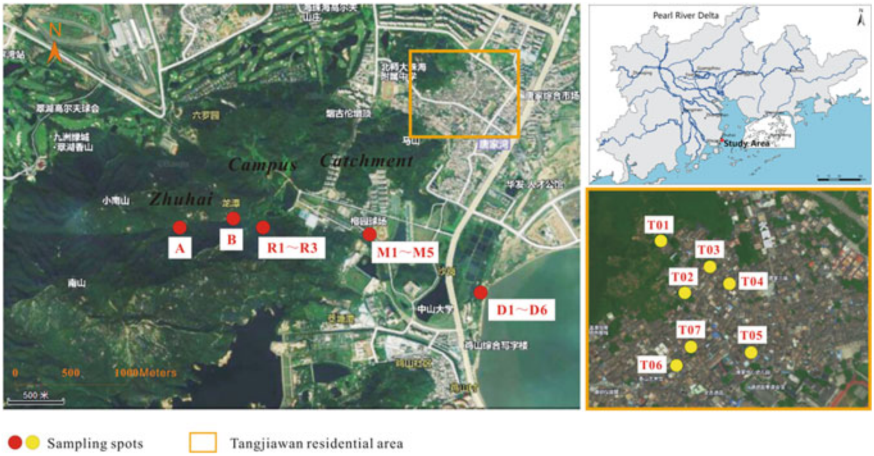


Fig. 10 Study areas and sampling sites (based on images from Google Earth)

Table 5 Observation wells in the Zhuhai Campus catchment

Area	Observation well	Depth/m	Type
Recharge	R1	4.2	Unconfined water
	R2	10	Base rock fissure water
	R3	13.2	Base rock fissure water
Middle	M1	5	Unconfined water
	M2	8.5	Confined water
	M3	10	Confined water
	M4	11.3	Confined water
	M5	17.8	Base rock fissure water
Discharge	D1	5	Unconfined water
	D2	8	Unconfined water
	D3	10	Unconfined water
	D4	15	Confined water
	D5	20	Confined water
	D6	34	Base rock fissure water

the Laboratory Center of Sun Yat-sen University, and bicarbonate by 0.01 NH_2SO_4 titration method.

3.2 Characteristics of Nitrogen and Phosphorus Pollution in Groundwater Under Minor Human Disturbance

The ZCSYSU, established in 2000 with around total 9000 students, had a relatively minor impact on the groundwater. N and P content in the groundwater (Table 6) indicated that NO_3^- was low, with a maximum concentration of only 4.11 mg/L. The NO_3^- concentration was higher in the wells of shallow unconfined aquifers, following the descending order of recharge area, discharge area, and middle area. NH_4^+ was similarly concentrated in shallow unconfined aquifer wells, following the descending order of middle area, discharge area, and recharge area, and with a maximum concentration of 4.74 mg/L in well M1. The NO_2^- and PO_4^{3-} concentrations were both relatively low, and did not differ greatly among the sites.

The dissolved inorganic N ($DIN = NO_3^- + NO_2^- + NH_4^+$) values were further analyzed using depth diagrams (Fig. 11), and the following results were obtained.

(1) The DIN concentration varied by groundwater types and showed an ascending order of unconfined water, confined water, and base rock fissure water. DIN pollution was largely concentrated in the shallow wells of unconfined waters (R1, M1, D1, and D2).

(2) For the shallow unconfined aquifer wells, the DIN contents were higher in the dry season than those in the rainy season, and showed a large variation. Low DIN was detected in the other wells with little seasonal variation. The lower concentrations in the wet season could be explained by a dilution process due to rainwater permeation and enhanced N consumption by microorganisms under higher temperatures (Jin et al. 2004).

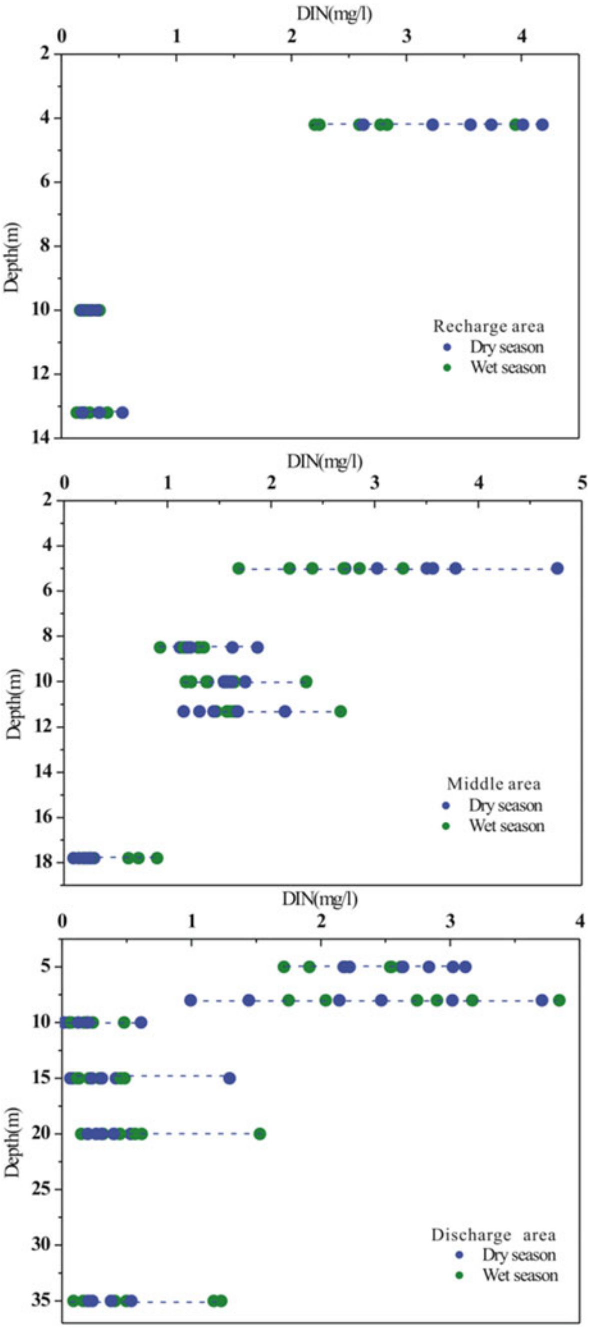
(3) The highest DIN concentration was found in the middle area and the lowest in the discharge area. The correlation analysis between DIN and its components, NO_3^- and NH_4^+ (Fig. 12) revealed a significant positive correlation between DIN and NO_3^- in the recharge area ($R = 0.99$), indicating that DIN principally existed as NO_3^-, particularly in the unconfined water of R1, where NO_3^- accounted for 94% of DIN. In the middle area, DIN was significantly correlated with NH_4^+ ($R = 0.98$), which accounted for 87.5% of DIN, exclusively in the unconfined water of M1 (97.7% of DIN). The composition was more complex in the discharge area, where DIN was largely present as NH_4^+ in D1 (92% of DIN), and as NO_3^- in D2 (76.8% of DIN), indicating the impact of nitrification.

Table 6 Characteristics of nitrogen and phosphorus pollution in groundwater at Zhuhai Campus, Sun Yat-sen University

Area	Well	Depth (m)	NO_3^- (mg/L)			NH_4^+ (mg/L)			NO_2^- (mg/L)			PO_4^{3-} (mg/L)		
			Max	Ave	Min	Max	Ave	Min	Max	Ave	Min	Max	Ave	Min
Recharge	R1	4.2	4.11	2.98	2.08	0.70	0.19	–	0.018	0.009	–	0.027	0.017	–
	R2	10	0.13	0.09	–	0.23	0.17	0.11	0.004	0.003	–	0.019	0.018	–
	R3	13.2	0.30	0.11	–	0.32	0.20	0.11	0.007	0.005	–	0.021	0.016	–
Middle	M1	5	0.13	0.09	–	4.75	2.98	1.69	0.009	0.005	–	0.024	0.018	–
	M2	8.5	0.94	0.19	–	1.54	1.16	0.85	0.006	0.004	–	0.019	0.016	–
	M3	10	0.65	0.15	–	1.66	1.44	1.09	0.090	0.013	–	0.021	0.017	–
	M4	11.3	0.68	0.18	–	2.67	1.57	0.92	0.007	0.004	–	0.024	0.017	–
	M5	17.8	0.83	0.31	–	0.54	0.16	0.03	0.005	0.003	–	0.027	0.018	–
Discharge	D1	5	1.35	0.25	–	3.01	2.27	1.28	0.005	0.004	–	0.021	0.014	–
	D2	8	3.64	2.11	0.08	0.90	0.37	0.05	0.155	0.040	–	0.024	0.017	–
	D3	10	0.55	0.20	–	0.48	0.10	–	0.027	0.012	–	0.019	0.017	–
	D4	15	1.17	0.31	–	0.18	0.09	–	0.013	0.008	–	0.021	0.015	–
	D5	20	1.50	0.28	–	0.48	0.22	0.03	0.005	0.004	–	0.024	0.021	–
	D6	35	1.05	0.48	–	0.43	0.17	0.06	0.004	0.004	–	0.019	0.016	–

Note "–" indicates the value is below the thresholds of detection, which are: NO_3^-: <0.05 mg/L; NH_4^+: <0.02 mg/L, NO_2^-: <0.003 mg/L, PO_4^{3-}: <0.01 mg/L

Fig. 11 Dissolved inorganic N concentrations in the groundwater sites of Zhuhai Campus



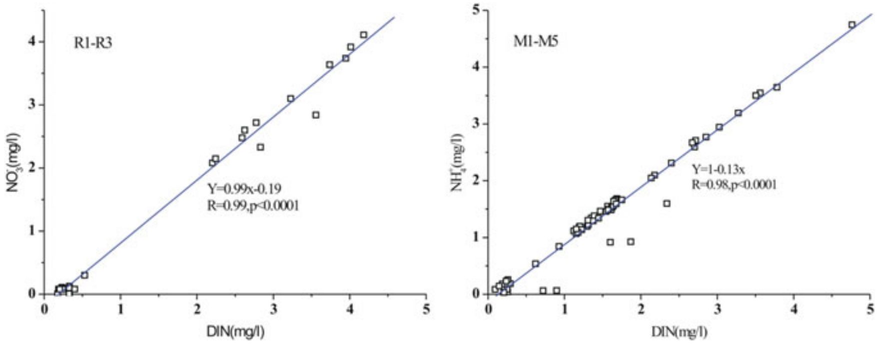


Fig. 12 Correlation between N forms and dissolved inorganic N in recharge and middle areas

3.3 Characteristics of Nitrogen and Phosphorus Pollution in Groundwater Under Conditions of Extensive Human Activity

Based on water samples collected from July 2009 to June 2010 (Table 7), the Tangjiawan residential area had significantly higher N and P contents in its groundwater than the ZCSYSU, with more N in particular. The NO_3^- concentration was between 9.51 and 151.3 mg/L, with an average as high as 87.6 mg/L. The NH_4^+ and NO_2^- contents were lower, and were not detected in some samples. The highest values of NH_4^+ and NO_2^- were 7.03 and 2.219 mg/L, respectively, which were both observed in well T04. The P content of the residential area was overall higher than that of the campus despite the similar geological settings, chiefly in wells T04 and T05, which had annual averages of 1.31 and 2.31 mg/L, respectively.

Due to the processes through which N migrates and transforms in saturated soils, N pollution of groundwater occurs largely in the form of NO_3^- (Chen et al. 2006a, b). At the Tangjiawan residential area, NO_3^- accounted for 83.0–99.0% of DIN. According to the World Health Organization, the maximum NO_3^- concentration allowed in domestic water is 10 mg N/L, and the value at all wells except T01 exceeded this threshold, indicating the status of severe N pollution. T01 is an old well built in 1599, located at the upper footslope within the local groundwater recharge area, which contributed to the lower degree of N pollution at this site. The NO_3^- content was much high downstream from T01. In wells T02, T04, and T05, the groundwater had NO_3^- concentrations of 33.5–88.2 mg/L. The concentrations in wells T03, T06, and T07 ranged from 103 to 151.3 mg/L. Large fluctuation in the rainy season was found compared to that in the dry season (Fig. 13). The Tangjiawan residential area is a historic area with a high building density, and a primitive and aging water drainage pipework that disposes human excreta mainly into cesspools. According to isotopic signals by Zhao et al. (2008) on groundwater NO_3^-, the main sources of N pollution in Tangjiawan were domestic water and seepage from cesspools. Complex variations in

Table 7 Groundwater nitrogen and phosphorus pollution in the Tangjiawan residential area

Well	NO_3^- (mg/L)			NH_4^+ (mg/L)			NO_2^- (mg/L)			PO_4^{3-} (mg/L)		
	Max	Ave	Min	Max	Ave	Min	Max	Ave	Min	Max	Ave	Min
T01	15.90	12.12	9.51	0.12	0.07	–	0.007	0.005	–	0.021	0.016	–
T02	85.50	74.61	59.80	0.35	0.15	–	0.017	0.011	–	0.030	0.022	–
T03	147.70	128.61	115.14	0.20	0.07	–	0.030	0.015	–	0.023	0.019	–
T04	83.00	59.12	33.50	7.03	2.32	0.09	2.219	0.263	0.007	2.308	1.310	0.292
T05	88.20	84.81	81.90	0.25	0.10	–	0.122	0.031	0.004	2.835	2.307	1.575
T06	151.30	135.38	121.40	0.37	0.11	0.02	0.202	0.050	0.004	0.196	0.098	0.047
T07	128.90	118.45	103.00	1.65	0.87	0.04	1.599	0.284	–	0.092	0.032	–

Note "–" indicates the value is below the thresholds of detection, which are: NO_3^-: <0.05 mg/L; NH_4^+: <0.02 mg/L, NO_2^-: <0.003 mg/L, PO_4^{3-}: <0.01 mg/L

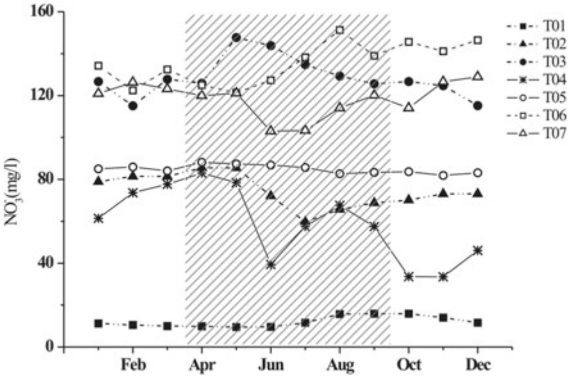


Fig. 13 Seasonal variation of NO^{3-} in the groundwater of the Tangjiawan residential area

NO_3^- concentration could be explained by a combination of increased seepage from rainwater, denitrification, and dilution (Zhao et al. 2008).

In comparison, the P content was relatively low. Figure 14a shows the seasonal P content in the wells, which, together with Table 7, indicates that the PO_4^{3-} concentrations were highly variable among the wells. Upstream wells T01, T02, T07, T06, and T03 had less PO_4^{3-}, and none of them had a concentration over 0.1 mg/L, except T06 (0.047–0.196 mg/L). Downstream wells T04 and T05 were more severely polluted with P, with maximum values of 2.31 mg/L and 2.84 mg/L, respectively, which are significantly higher than those in the campus (maximum: 0.027 mg/L). Figure 14b shows the seasonal variation of PO_4^{3-}. PO_4^{3-} was not detected in wells T01, T02, T03, or T07 in May, possibly due to the dilution of groundwater by rainfalls. Being situated in a more polluted area, T04 showed great PO_4^{3-} fluctuations, with the lowest values in April and August. The PO_4^{3-} content was more stable in T05. Domestic wastewater and animal excreta contain high NH_4^+ and inorganic P concentrations (Xing et al. 2001). Since well T04 was located only 1–2 m from a cesspool, its high NH_4^+ and PO_4^{3-} concentrations could be attributed to seepage of domestic wastewater and excreta. The highest PO_4^{3-} content was found in well T05, which was located at the lowest altitude and situated 1–2 m from a cesspool in an area with frequent human activities (e.g., clothes washing).

As shown by the presence of numerous wells, groundwater used to be an important source of drinking water for Tangjiawan residents, who still collect water from some wells for washing food ingredients and clothes. The Campus catchment can be considered as a reasonable background site for Tangjiawan, representing the conditions of the local groundwater in earlier days. Therefore, it is likely that the local groundwater in Tangjiawan became heavily polluted with N and P due to human activities over hundreds of years.

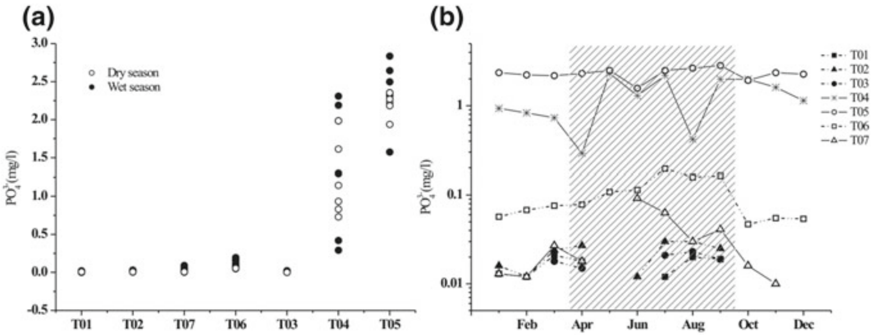


Fig. 14 Spatial distribution (**a**) and seasonal variation (**b**) of groundwater PO_4^{3-} in the Tangjiawan residential area

4 Case Study: Trace Metal Pollution in the Shima River

4.1 Study Area

Dongguan is located at the central Guangdong Province (113°31′–114°15′E, 22°39′–23°09′N) (Fig. 15), and has a subtropical monsoon climate with an annual average rainfall of 1,954 mm and an average temperature of 22.9 °C. Typhoons occur frequently from June to September, and rainstorms occur regularly. Dongguan has an area of 2,465 km^2, and higher and lower terrain is distributed in the southeast and northwest areas of the city, respectively. Dongguan is covered with unconsolidated quaternary clay soil that is thick from 0 to 18 m (Gao et al. 2015a). Hills and alluvial plains are the primary terrain, accounting for 88% of the total area of Dongguan (Wu et al. 2015). Dongguan underwent a transition from agricultural to an industrial and technological economy after Xiaoping Deng's Southern Tour in 1992. Since then, the residential population and the GDP have increased more than 3.7 and 57 times from 1992 to 2015 (Dongguan Bureau of Statistics 1978–2015), respectively.

The Shima River is the largest tributary of the Dong River in Dongguan (Fig. 15). Originating from the Baoan District in Shenzhen, the Shima River is 88 km in length with a watershed area of 1,249 km^2. Its original flow direction was from south to north, draining through an outlet located at Qiaotou town into the Dong River that is a crucial water source for the PRD region. Because of the demand of potable water from Hong Kong, eight pumping stations were installed along the Shima River as the major component of the diversion project in 1964 to supply freshwater from the Dong River to Hong Kong, resulting in the reversal of the river flow direction (Gao et al. 2017). The Shima River provided approximately 80% of Hong Kong's potable water use after the completion of the expansion project in 1987 (Xu 2006). Rapid industrial development and the population increase in Dongguan since 1990s have resulted in huge water demand. In 2003, the Quondam Diversion Project was substituted by a closed pipeline continually transporting water to Hong Kong, thus recovering its

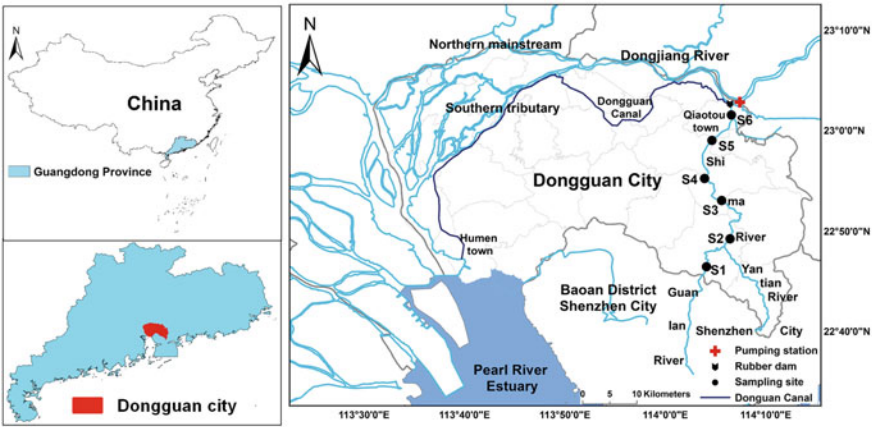


Fig. 15 Study area and sampling sites

original south-to-north flow direction. River water containing high concentrations of pollutants (e.g., trace metals) began to drain into the Dong River. Moreover, a rubber dam with a length of 92 m and height of 2.35 m was built at the outlet at Qiaotouto minimize contaminant discharge. In the dry season, the river water flows into the Dongguan Canal through an underground pipe, eventually draining through Humen into the estuary. However, the rubber dam may collapse during heavy rainfalls.

River water (S1–S6) was collected using the grab-sampling method in February, June, and November 2012. Water samples collected were stored in a refrigerator (4 °C) in the dark after being transported to the laboratory, and then were filtered through a polypropylene membrane with a diameter of 0.45 μm. Levels of metals or metalloid [zinc (Zn), cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), lead (Pb), manganese (Mn), iron (Fe), and arsenic (As)] were determined using inductively coupled plasma–atomic emission spectrometry (ICP-AES; IRIS, Pleasant Prairie, WI, USA). The detection limits were 10 μg/L for Cu, Cr, Ni, and As, 5 μg/L for Zn, Mn, Pb, and Fe, and 1 μg/L for Cd.

Surface sediments were collected and stored at −40 °C in the dark after being transferred to the laboratory. Sediment sample was ground using an agate mortar and homogenized until all sediment particles passed through a 100 mesh nylon sieve after freeze-drying. Approximately 50 mg of sediment sample was totally digested in a HF-HNO_3 mixture, under high temperature and pressure conditions, in Teflon tubes for the determination of trace metal (Cd, Zn, Cu, Ni, Cr, Pb, As, scandium (Sc), and vanadium (V)) concentrations with inductively coupled plasma-mass spectrometry (ICP-MS, X-2; Thermo, Waltham, MA, USA). Fe, aluminum (Al), and Mn concentrations in the digestion mixture were measured using ICP-AES.

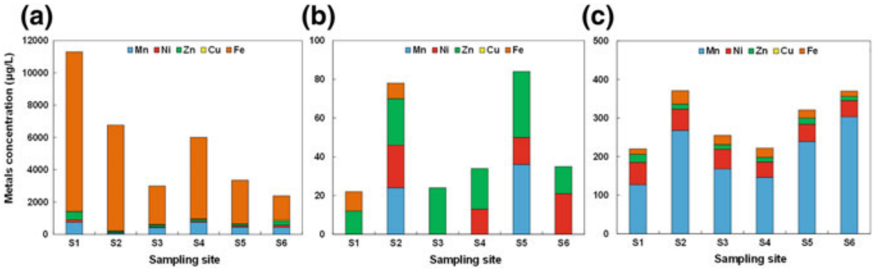


Fig. 16 Concentration of dissolved trace metals in river water in February (**a**), June (**b**), and November (**c**), 2012

4.2 Trace Metal Pollution in River Water

Rapid urbanization and industrialization processes have resulted in the release of large quantities of pollutants (e.g., trace metals, nutrients, etc.) into the environment, leading to severe pollution in surface water bodies in Dongguan (Xiong et al. 2010; Liu et al. 2011a, b). Moreover, the Shima River has suffered from intense human activities, resulting in a number of environmental issues (Gao et al. 2014, 2015b; Jiang et al. 2016). Total trace metal concentrations showed a clear spatiotemporal difference, decreasing from site S1 (11,302 μg/L) to S6 (2,386 μg/L) in February (Fig. 16a), which likely resulted from deposition following the adsorption of trace metals onto suspended particles (Varol and Şen 2012). Meanwhile, a slight increasing trend in metal concentrations was observed in June and November (Fig. 16b, c), which was likely associated with the confluence of river branches, such as the Yantian River, before site S2 and wastewater discharge along the river channel. Total trace metal concentrations in river water generally followed the descending order of February, November, and June, as more monthly precipitation was observed in June (256 mm) and November (168 mm) than February (51.2 mm). A dilution effect via precipitation was the main cause of the relatively lower concentration of trace metals in the rainy season in the Shima River.

In terms of individual metals, As, Cr, Cd and Pb, with detection limits of 10, 10, 1, and 5 μg/L, respectively, were not observed in the river water during the three investigated periods (Table 8). The highest observed concentrations were 748 μg/L for Mn, 151 μg/L for Ni, 494 μg/L for Zn, and 9,860 μg/L for Fe at site S1 in February, which substantially exceeded the national surface water quality standard (MEP 2002). This suggested that a large number of trace metals originated from upstream, in particular from the industrial wastewater discharge in Baoan District, Shenzhen city. In November, the trace metal concentrations, with the exception of Mn, of all water samples met the drinking water quality standards (MEP 2002; WHO 2011). Mn pollution likely promoted the occurrence of brown/black precipitate (Koukal et al. 2004), causing unsightly stains in the river water in February and November. Overall, river water pollution caused by trace metals might present a serious risk to urban

Table 8 Trace metal concentrations of the river water samples (μg/L)

Site	**As**	**Cd**	**Cr**	**Pb**	**Mn**	**Ni**	**Zn**	**Cu**	**Fe**
February									
S1	n.d.	n.d.	n.d.	n.d.	748	151	494	49.0	9860
S2	n.d.	n.d.	n.d.	n.d.	84.0	30.0	85.0	18.0	6550
S3	n.d.	n.d.	n.d.	n.d.	420	52.0	116	25.0	2390
S4	n.d.	n.d.	n.d.	n.d.	749	61.0	119	28.0	5050
S5	n.d.	n.d.	n.d.	n.d.	443	80.0	104	24.0	2700
S6	n.d.	n.d.	n.d.	n.d.	436	130	247	93.0	1480
June									
S1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12.0	n.d.	10.0
S2	n.d.	n.d.	n.d.	n.d.	24.0	22.0	24.0	n.d.	8.00
S3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24.0	n.d.	n.d.
S4	n.d.	n.d.	n.d.	n.d.	n.d.	13.0	21.0	n.d.	n.d.
S5	n.d.	n.d.	n.d.	n.d.	36.0	14.0	34.0	n.d.	n.d.
S6	n.d.	n.d.	n.d.	n.d.	n.d.	21.0	14.0	n.d.	n.d.
November									
S1	n.d.	n.d.	n.d.	n.d.	127	58.0	21.0	n.d.	14.0
S2	n.d.	n.d.	n.d.	n.d.	268	55.0	13.0	n.d.	35.0
S3	n.d.	n.d.	n.d.	n.d.	168	51.0	12.0	n.d.	24.0
S4	n.d.	n.d.	n.d.	n.d.	146	40.0	12.0	n.d.	24.0
S5	n.d.	n.d.	n.d.	n.d.	239	45.0	16.0	n.d.	21.0
S6	n.d.	n.d.	n.d.	n.d.	303	42.0	11.0	n.d.	14.0
MEPC[a]	50	1	10	10	100	n.i.	50	10	300
MEPC[b]	100	10	100	100	n.i.	n.i.	2000	1000	n.i.
WHO[c]									

n.d. not detected
[a,b]Environmental quality standard (Class I and V) for surface water of China (MEP 2002)
[c]Guidelines for drinking-water quality-Forth edition (WHO 2011)

residents by polluting the local water supply as a result of the short distance between the water source area and the drainage outlet of the Shima River (Fig. 15) (Table 9).

4.3 *Trace Metal Pollution in Riverine Sediment*

Riverine sediment, a primary component of river ecosystems, not only is a sink for suspended solid and soluble chemicals originated from both natural sources and anthropogenic inputs into watersheds, but also is an important source due to the resuspension of deposited substances into the overlaying water (Hou et al. 2013).

Table 9 Trace metal concentrations in sediment cores from the Shima River (mg/kg)

Site	**V**	**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**	Mn	Fe	Al	Sc
S1	41.4	101	100	127	972	6.62	1.35	65.3	626	40327	87631	9.502
S2	59.8	279	216	271	1310	11.1	1.88	71.9	893	47458	96945	10.8
S3	54.3	335	181	401	1370	12.8	1.64	131	849	40562	102183	10.7
S4	59.6	469	253	630	1704	14.3	1.91	109	803	41395	99618	10.2
S6	73.8	50.2	24.7	26.3	92.6	13.3	0.504	47.3	283	38389	91945	13.0
BGV	65.3	50.5	14.4	17	47.3	8.9	0.056	36	279	24200	72100	12.2

BGV environmental background value for soils of Guangdong Province (China National Environmental Monitoring Centre 1990)

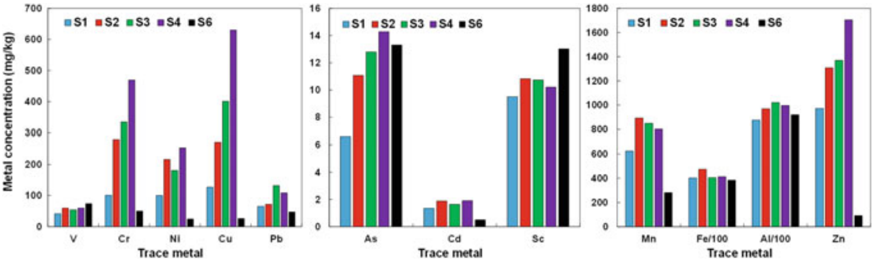


Fig. 17 Distribution of trace metal concentrations in riverine sediment of the Shima River

Generally, trace metals input into river systems tends to deposit on riverbeds after adsorption onto suspended particles and accumulation in sediments. In the dry season (February), the trace metal concentrations in the river water decreased from the upper reach site (S1) to the lower reach site (S6), whereas their concentrations in the surface sediment increased from site S1 to S4 along the river channel. This was in line with general sedimentation processes of trace metals in river systems. The metal concentrations were in the range of 41.4–73.8 mg/kg for V, 6.62–14.3 mg/kg for As, 9.50–13.0 mg/kg for Sc, 38.4–47.5 g/kg for Fe, and 87.6–102 g/kg for Al (Fig. 17), which were similar to the soil background values in Guangdong Province (China National Environmental Monitoring Centre 1990). Meanwhile, Cr, Ni, Cu, Zn, Cd, Pb, and Mn concentrations had mean values of 247, 155, 291, 1,089, 1.46, 85.0, and 690 mg/kg, respectively, which were substantially higher than local soil background values. Notably, Cr, Ni, Cu, Pb, Cd, Mn, and Zn concentrations decreased steeply at site S6, which was likely attributable to periodic dredging of sediment at the rubber dam.

To further assess the pollution level of each metal in the surface sediment, the geoaccumulation index (I_{geo}) was applied. The mean I_{geo} values were −0.786 for V, −0.179 for Al, −0.761 for Sc, and −0.250 for As, indicative of an uncontaminated status (Fig. 18). However, the mean I_{geo} values ranged from 0.194 to 0.559 for Pb, Mn, and Fe, indicating that they were uncontaminated-to-moderately contaminated elements. Cr had a mean I_{geo} value of 1.30, indicative of moderate contamination, and the mean I_{geo} values of Ni, Cu, Zn, and Cd fell in the range of 2–4, suggesting moderate-to-heavy contamination. The highest I_{geo} value was obtained for Cd (3.97), due mainly to a low background value and higher concentration in the sediments. Overall, the pollution status of individual metals based on the average I_{geo} values followed a descending order of Cd, Zn, Cu, Ni, Cr, Mn, Pb, Fe, Al, As, Sc, and V.

Hierarchical cluster analysis was conducted for the I_{geo} values of determined trace metals to preliminarily differentiate the sources of the sediment metals according to the pollution level and path. Cluster A included uncontaminated or slightly contaminated metals, including V, Sc, Al, As, and Fe. These metals in sediment were likely derived from parent materials due to the similarity between their concentrations and local soil background levels (Fig. 19). Trace metals clustered in groups B and C were the main pollution elements, and were identified as anthropogenic components (Bai

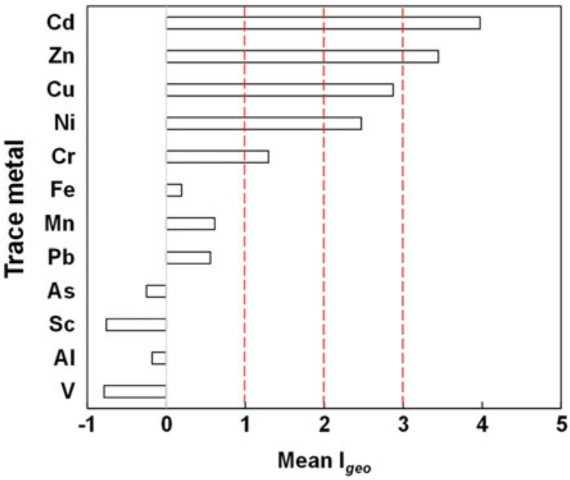


Fig. 18 Mean geoaccumulation index (Igeo) values of the trace metals in sediment

et al. 2011; Fu et al. 2014; Ma et al. 2016). Overall, coal and leaded-gasoline were found to be the major sources for sediment Pb in the highly urbanized catchment in China (Li et al. 2012), however, since the phase-out of leaded gasoline in 1999, coal was mainly responsible for Pb pollution in the aquatic environment (Zhang et al. 2016). Furthermore, Cr can be found in stainless and alloy steels manufacturing industries (Yeung et al. 2003). Whereas Mn might have originated from metal mining and smelting (Fu et al. 2014). In cluster C, Ni, Cu, Zn, and Cd showed moderate-to-heavy contamination in sediment. Effluents from machinery, electronics, and electroplating industries reportedly contain large quantities of Zn, Ni, and Cu in highly urbanized catchment (Li et al. 2013; Iqbal et al. 2015). This was in good agreement with the conditions in the Shima River catchment, where Cu, Ni, and Zn concentrations in river water decreased from sites S1 to S6 in February, suggesting that upstream industrial areas contributed to both river water and sediment pollution. However, Cd was likely associated with non-point pollution sources, because its concentrations were significantly lower in sediments than those in riparian soils ranging from 2.00 to 11.2 mg/kg along the Shima River (Gao et al. 2014), which was mainly indicative of agricultural runoff. Furthermore, soil Cd pollution was found to be associated mainly with the application of fertilizer (Cai et al. 2008). Consequently, the trace metals included in cluster B and C were mainly associated with industrial and agricultural activities.

5 Conclusions

The PRD region had experienced a significant increase in population and economic growth over the past several decades. To fully apprehend the effects of rapid development on the ecological environment in this region, three case studies regarding

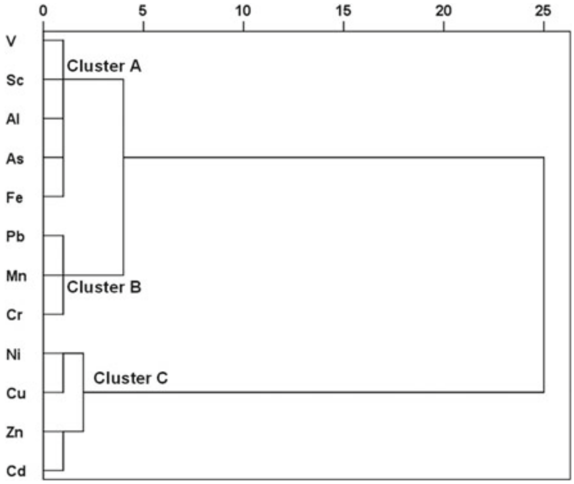


Fig. 19 Dendrogram of trace metals based on the geoaccumulation index (Igeo) in sediment samples

nutrients and trace metals pollution in different environmental settings have been conducted.

The total N input and output of the PRD showed little variations during the investigated periods, whereas the N surplus increased significantly. The rapid urbanization and intensive human activities exerted significant impacts on the evolution of nitrogen budgets during 2000–2010, indicating a severer N pollution in Guangzhou, Zhuhai, Shenzhen, Dongguan, and Foshan. On the contrary, the phosphorus input and output varied distinctly during 2000–2010. The major source of P input was found to be human and livestock excreta, which was followed by the application of fertilizer, and the crop harvests were mainly responsible for the P output. A high phosphorus surplus per unit area in Shenzhen, Dongguan, Foshan, Guangzhou, and Zhongshan city reflected a great risk of P-related pollution. In terms of nutrients pollution in the groundwater, DIN dominated by NO_3^- and/or NH_4^+ was highly concentrated in the shallow unconfined aquifer from the Zhuhai Campus of Sun Yat-sen University. It was notable that N and P concentrations in the groundwater were found to be higher in Tangjiawan residential area than in Zhuhai Campus, directly revealing the significant impacts of domestic wastewater on the groundwater systems.

The severe trace metals pollution had been observed in the highly urbanized Shima River catchment area. The river water pollution with high concentrations of trace metals in the dry season likely imposed obvious threats on the drinking water resource area. According to cluster analysis of metals, sediment V, Sc, Al, As, and Fe were derived from the parent materials. And industrial activities likely contributed significantly to sediment Pb, Cr, Ni, Cu, Zn, and Mn. However, Cd was supposed to be related to non-point pollution source. Riverine sediment polluted by Cr, Ni, Cu, Zn, and Cd likely resulted in the secondary pollution of river water due to its re-suspension during the flood processes.

It was evident that the rapid urbanization, industrialization and intensive human activities significantly affected surface water and groundwater, resulting in some hazards to the safety of urban water consumption in the PRD region. Thus, the improvement of water quality necessitates the implementation of pollution prevention measures, the control of agrochemical application, and the reduction of industrial wastewater discharge. Furthermore, we urge the local governments to carry out the dredging project in the polluted river channel near the water source areas.

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