water

MDPI

Article

Hydrogeochemical Characteristics and Groundwater Quality in a Coastal Urbanized Area, South China: Impact of Land Use

Chunyan Liu [1,2], Qinxuan Hou [1,2,*], Yetao Chen [3] and Guanxing Huang [1,*]

1 Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang 050061, China
2 Hebei Key Laboratory of Groundwater Remediation, Shijiazhuang 050061, China
3 Hebei Huanxue Environmental Protection Technology Company Limited, Shijiazhuang 050000, China
* Correspondence: houqinxuan@163.com (Q.H.); huangguanxing2004@126.com (G.H.)

Abstract: Land use transformation accompanied with various human activities affects groundwater chemistry and quality globally, especially in coastal urbanized areas because of complex human activities. This study investigated the impact of land use on groundwater chemistry and quality in a coastal alluvial aquifer (CAA) of the Pearl River Delta where urbanization continues. A fuzzy synthetic evaluation method was used to evaluate the groundwater quality. Besides, factors controlling groundwater chemistry and quality in the CAA were discussed by using a principal components analysis (PCA). Nearly 150 groundwater samples were collected. All samples were filtered on-site and stored at 4 °C until the laboratory procedures could be performed. Nineteen chemical parameters including pH, dissolved oxygen, redox potential, total dissolved solids, K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, HCO_3^-, NO_3^-, SO_4^{2-}, Cl^-, I^-, NO_2^-, Pb, Mn, Fe, and As were analyzed. Results show that groundwater chemistry in the CAA was dominated by Ca-HCO_3 and Ca·Na-HCO_3 facies. In addition, groundwater with NO_3 facies was also present because of more intensive human activities. In the CAA, 61.8% of groundwaters were fit for drinking, and 10.7% of groundwaters were undrinkable but fit for irrigation, whereas 27.5% of groundwaters were unfit for any purpose. Poor-quality groundwaters in urban and agricultural areas were 1.1–1.2 times those in peri-urban areas, but absent in the remaining area. Groundwater chemistry and quality in the CAA was mainly controlled by five factors according to the PCA. Factor 1 is the release of salt and NH_4^+ from marine sediments, and the infiltration of domestic and septic sewage. Factor 2 is agricultural activities related to the irrigation of river water, and the use of chemical fertilizers. Factor 3 is the industrial pollution related to heavy metals and acid deposition. Factor 4 is the input of anthropogenic reducing sewage inducing the reductive dissolution of As-loaded Fe minerals and denitrification. Factor 5 is the I^- contamination from both of geogenic and anthropogenic sources. Therefore, in order to protect groundwater quality in coastal urbanized areas, repairing old sewer systems in urban areas, building sewer systems in peri-urban areas, limiting sewage irrigation and the amount of chemical fertilizers application in agricultural areas, as well as strengthening the supervision of the industrial exhaust gas discharge in urban and peri-urban areas are recommended.

Keywords: groundwater chemistry; groundwater quality; coastal aquifers; land use; factors

Citation: Liu, C.; Hou, Q.; Chen, Y.; Huang, G. Hydrogeochemical Characteristics and Groundwater Quality in a Coastal Urbanized Area, South China: Impact of Land Use. *Water* **2022**, *14*, 4131. https://doi.org/10.3390/w14244131

Academic Editors: Zbigniew Kabala and Dimitrios E. Alexakis

Received: 31 October 2022
Accepted: 15 December 2022
Published: 19 December 2022

1. Introduction

The large scale transformation of agricultural and natural ecosystems to urbanization is one of huge anthropogenic impacts on the groundwater environment [1]. Large-scale urbanization in China has lasted for several decades, especially in coastal areas. For example, the population in urban areas in China shows a pattern, being high in coastal areas and low in inland areas on a national scale [2], because coastal areas connecting the inland and oceans in the earth system are crucial zones, and play an important role for social and economic development. To date, more than two billion people live in coastal areas globally, and the groundwater resource is one of the major sources to supply drinking water for around one billion people in these areas [3]. On the other hand, because of the transformation of agricultural and natural ecosystems to urbanized areas, accompanied by various kinds of human activities [4,5], groundwater chemistry and quality issues are becoming increasingly serious, and threatening drinking water security in coastal areas worldwide [6–9]. For example, Han and Currell reviewed how urban growth and water transfer projects may be responsible for changes observed in coastal groundwater quality in China [10]. Sellamuthu et al. reported that groundwater salinization and nitrate pollution was highly influenced by anthropogenic sources in a rapidly developing urban area in India [11]. As a consequence, it is necessary to investigate the impact of land use transformation from agricultural and natural ecosystems to urbanization on groundwater chemistry and quality in coastal areas [12,13], and to provide suggestions for the protection and management of groundwater resource.

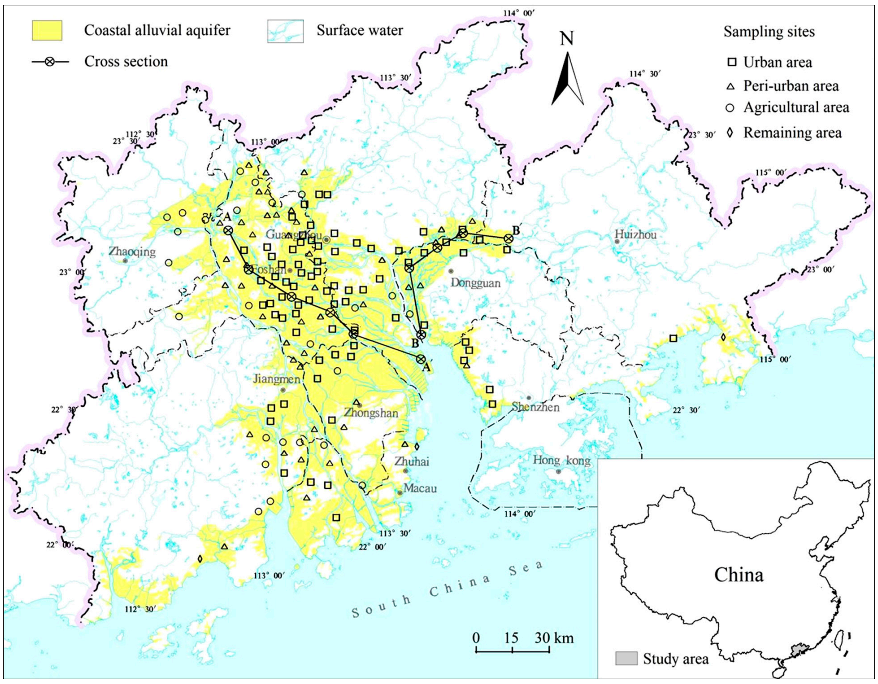
The Pearl River Delta (PRD), adjacent to the South China Sea, is one of the largest coastal urbanized areas in China. The expansion of urbanization in this area has lasted for more than four decades, and land-use change in this area is mainly conversion from agricultural lands to urban areas. For instance, the urban area in the PRD in 2018 was approximately two times and three times of that in 2006 and 1998, respectively [14]. On one hand, urbanization accompanied with a huge influx of population results in the increased importance of groundwater resource in the PRD than before [15]. On the other hand, urbanization accompanied with various human activities has deteriorated not only surface water quality but also shallow groundwater quality in this area [16]. To date, many groundwater environmental issues in this area, such as nitrate and phosphate pollution, and iodine and manganese contamination, had already received attention [17–20]. However, shallow groundwater in the coastal alluvial aquifer is a major source for water supply in this area [21], but knowledge on the influence of large-scale land use conversion on groundwater chemistry and quality in this coastal alluvial aquifer is still limited.

Therefore, the present study aims to analyze the impact of land use on shallow groundwater quality and the hydrogeochemical characteristics of the coastal alluvial aquifer of the PRD, and to discuss factors controlling groundwater chemistry and quality in this coastal alluvial aquifer. Here, a fuzzy synthetic evaluation method (FSEM) combined with the groundwater quality standards of China was used for evaluating groundwater quality in this study [16,22]. The results will contribute to the development and utilization of groundwater resource in the PRD.

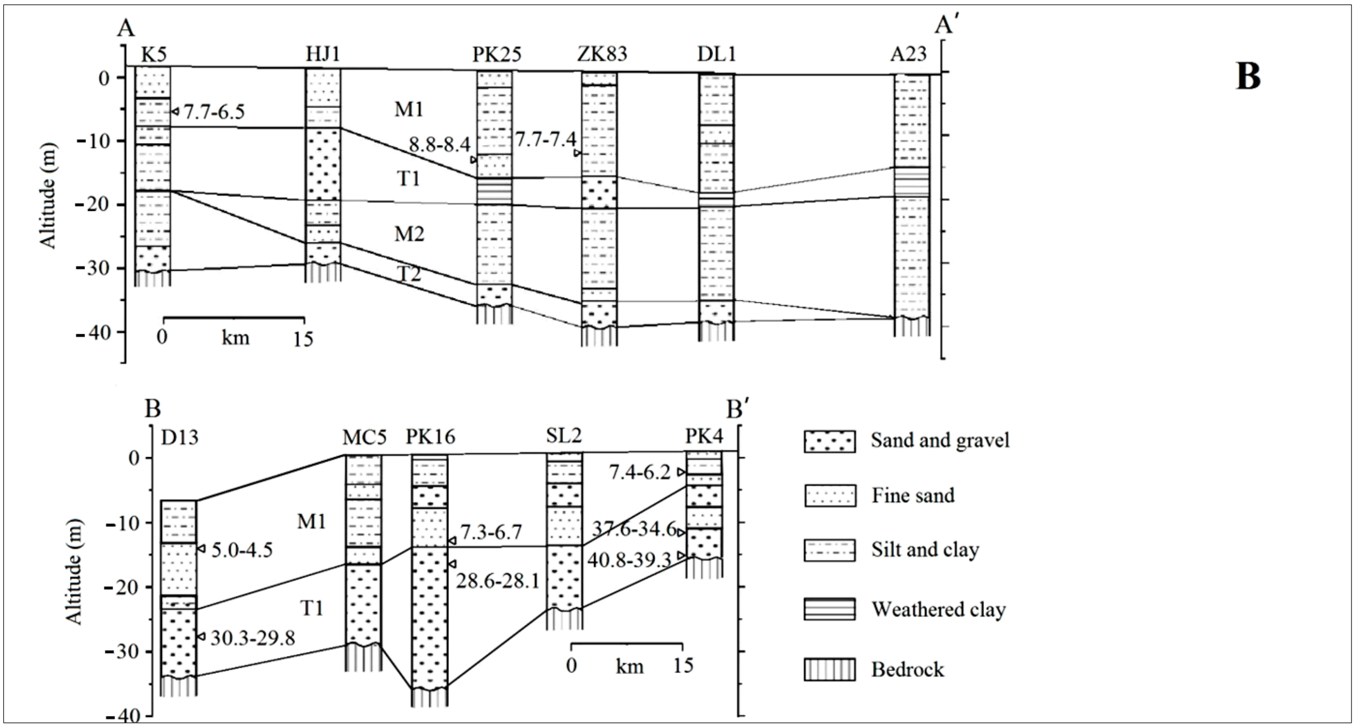
2. Study Area

2.1. Geographical and Hydrogeological Settings

The PRD is located in the southern Guangdong Province of China and covers a total area of about 42 thousand km^2 (Figure 1). It is adjacent to the South China Sea in the south and surrounded by hills in the east, west, and north. The climate is typically subtropical marine monsoon and the average annual rainfall and temperature are 1600–2300 mm and 21.4–22.4 °C, respectively [21]. The wet season is from April to September. Three main rivers such as Dongjiang River, Xijiang River, and Beijiang River merge into the Pearl River system and finally discharge into the South China Sea [21]. The PRD can be divided into four groundwater units: coastal alluvial aquifer, alluvial-proluvial aquifer, fissured aquifer, and karst aquifer [23]. As a major aquifer for water supply, the coastal alluvial aquifer is widely distributed in the PRD plain and covers a total area of 8837 km^2 (Figure 1). The Quaternary strata of this area consist of two marine formations and two continental formations. The young marine formation was deposited in the Holocene period and dominated by silt and clay, except the top layer, in which sand is often dominant [24]. The old marine formation and two continental formations were deposited in the Pleistocene. In the former, silt and clay are dominant, whereas the latter two are commonly dominated by sand and gravel [24]. The coastal alluvial aquifer consists of sand/gravel layers in continental formations and the young marine formation. Note that shallow groundwater occurs in sand layers of young marine and continental formations [25]. Shallow groundwater in the coastal alluvial aquifer is mainly recharged by precipitation, agricultural irrigation, and various river waters, and finally discharges into the South China Sea [25]. In addition, shallow groundwater near coastal lines is also often intruded by sea water [26].



(**A**)



(**B**)

Figure 1. Hydrogeological setting and sampling sites in the coastal alluvial aquifer of the Pearl River Delta. (**A**) Sampling sites. (**B**) Cross sections.

2.2. Land Use and Human Activity Characteristics

Overlying the coastal alluvial aquifer, the urbanized area had increased to approximately 2300 km^2 in 2006 and accounted for more than one fourth of the total area [27]. The study area can be divided into four areas according to the land use, that is, urban areas (UA), peri-urban areas (PUA), agricultural areas (AA), as well as the remaining area (RA) (Figure 2). UA are large-scale urbanized areas with a high intensity of population and factories [27]. The term PUA refers to regions ~2 km outside of urban areas with a high population and small factories but lacking a sewer system [18]. AA refers to cultivated lands and garden plots, and sometimes sewage irrigation occurs [21]. The RA include surface water bodies, small villages, woodlands, grasslands, and uncultivated lands where human activities are few [14]. The intensity of human activities qualitatively follows the order of UA > PUA > AA > RA [28].

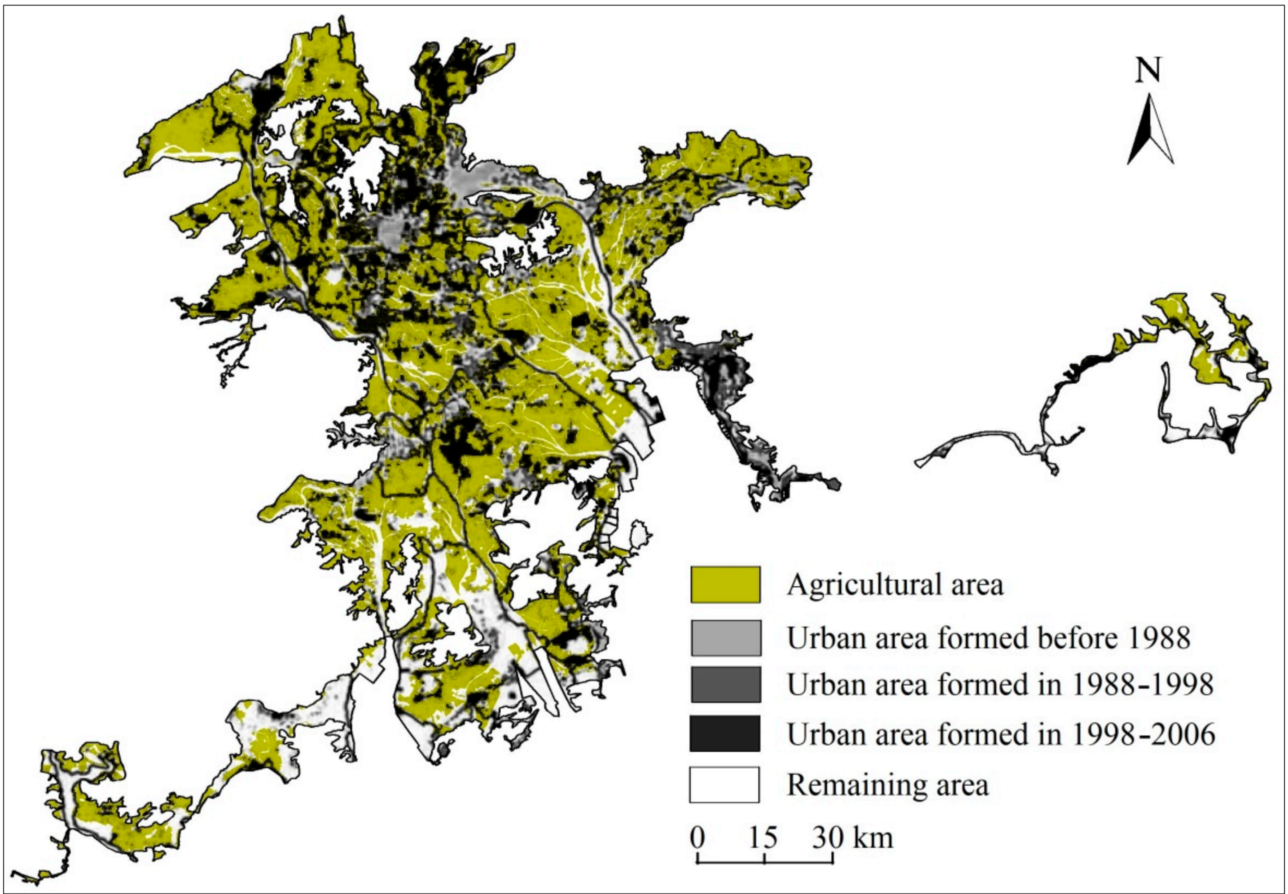


Figure 2. Spatial distribution of land-use types covering the coastal alluvial aquifer of the Pearl River Delta (data related to agricultural land and urbanized areas from [21,27], respectively).

3. Materials and Methods

3.1. Sampling and Analysis

A total of 149 shallow groundwater samples were collected from the coastal alluvial aquifer in the period from August to September of 2006–2007, and the sampling density was 10–20 samples/1000 km^2. Among them, 75 samples, 46 samples, 25 samples, and 3 samples were collected from UA, PUA, AA, and RA, respectively. Three parameters including pH, dissolved oxygen (DO), and redox potential (Eh) were measured on-site using a multi-parameter instrument (WTW Multi 340i/SET, Germany) that was calibrated before measurements were taken. A further 16 parameters, including total dissolved solids (TDS), 5 cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, and NH_4^+), 6 anions (HCO_3^-, NO_3^-, SO_4^{2-}, Cl^-,

I^-, and NO_2^-), and 4 heavy metal(loid)s (Pb, Mn, Fe, and As) in samples were measured in the laboratory. Details for sampling, analysis, and quality control are shown in Section 3.1 of the supplementary material (SM).

3.2. Fuzzy Synthetic Evaluation Method (FSEM)

The FSEM is a common method to overcome the imprecision in the evaluation of groundwater quality [16]. In this study, combining with the groundwater quality standards of China (Table S1) [22], a fuzzy membership function was used to evaluate groundwater quality. Groundwater quality indicators referred to Mn, Fe, NH4+, As, I−, NO3−, TDS, NO2−, Cl−, Na+, Pb, and SO42−. Details are in Section 3.2 of the supplementary material (SM).

3.3. Principal Components Analysis (PCA)

The PCA is a powerful tool for analyzing high-dimensional hydrochemical data sets and reducing a large number of variables to a small number of principal components (PCs) by linearly combining measurements made on the original variables [29]. This multi-step method has been applied successfully to extract PCs and infer the underlying natural and/or anthropogenic processes that control the groundwater chemistry [28,30]. Therefore, in this study, using the software SPSS® Version 23.0 (SPSS Inc., Chicago, IL, USA), the PCA was carried out to reduce hydrochemical datasets of the coastal alluvial aquifer and extract the PCs, and infer the main factors controlling groundwater chemistry and quality in this aquifer. Note that the data below the detection limits were substituted with zero when data of chemical parameters in groundwaters were used for PCA. In the PCA, log-transformed data and a standardized data matrix were used to give each variable equal weight in the multivariate statistical analysis [30]. Rotation of the PCs was carried out using the Varimax method, and PCs with eigenvalues > 1 were retained for analyses. Kaiser–Meyer–Olkin and Bartlett's tests showed significant difference between the correlation coefficient matrix and identity matrix and were suitable for the PCA (Table S2). The absolute PC loadings of >0.75, 0.75–0.5, and 0.5–0.3 were denoted as strong, moderate, and weak, respectively.

4. Results

4.1. Hydrogeochemical Characteristics in the Coastal Alluvial Aquifer

The descriptive statistics for the concentrations of physicochemical parameters in groundwater in the coastal alluvial aquifer are shown in Table 1. Groundwater pH showed acidic to near-neutral values, with the median value of 6.8. DO and Eh values in groundwater showed wide ranges of 0.6–8.2 mg/L and −36–275 mV, respectively. The median concentrations of major cations showed an order of $Ca^{2+} > Na^+ > K^+ > Mg^{2+}$, whereas the median values of $HCO_3^- > Cl^- \approx SO_4^{2-} > NO_3^-$. Groundwater TDS concentrations also showed a wide range of 45–3353 mg/L with the median value of 568 mg/L. Two other nitrogen compounds, NH_4^+ and NO_2^-, were up to 60 mg/L and 33.3 mg/L, respectively, with median concentrations of 0.04 mg/L and 0.03 mg/L, respectively. Groundwater Fe and Mn concentrations were also abnormally high, up to 26.2 mg/L and 7.38 mg/L, respectively, with median concentrations of 0.11 mg/L and 0.12 mg/L, respectively. By contrast, two other heavy metal(loid)s in the groundwater, As and Pb, showed median concentrations of 0.004 mg/L and 0.001 mg/L, respectively. Additionally, groundwater I^- concentrations ranged from below the detection limit to 0.76 mg/L.

Table 1. Descriptive statistics of concentrations of chemical parameters in groundwater of the coastal alluvial aquifer in the Pearl River Delta.

Item	AL	Total Area				Urban Area			Peri-Urban Area			Agricultural Area			Remaining Area		
		Min.	Med.	Max.	PAL (%)	Min.	Med.	Max.	Min.	Med.	Max.	Min.	Med.	Max.	Min.	Med.	Max.
pH		3.5	6.8	7.6		4.4	6.9	7.5	3.5	6.6	7.3	4.7	6.5	7.6	5.5	6.1	6.3
DO (mg/L)		0.6	2.8	8.2		0.6	2.6	8.2	1.2	2.9	5.9	1.4	3.3	6.9	3.1	4.4	5.7
Eh (mV)		−36	17	275		−34	2	221	−26	24	275	−36	67	275	33	51	76
K^+ (mg/L)		<DL	20	88		1	23	88	<DL	14	71	1	22	44	2	12	22
Ca^{2+} (mg/L)		2	79	165		13	95	165	2	75	142	4	48	99	7	19	21
Mg^{2+} (mg/L)		<DL	8	118		1	9	54	<DL	8	94	1	7	118	3	5	9
HCO_3^- (mg/L)		<DL	248	641		3	295	641	<DL	187	616	6	147	459	20	45	55
TDS (mg/L)	1000	45	568	3353	6.7	88	704	1420	45	527	3353	56	406	3152	123	182	208
Cl^- (mg/L)	250	5	50	1631	5.4	8	55	390	5	43	1631	5	37	1620	8	21	35
NO_3^- (mg/L)	88.9	0.3	22.6	184.9	10.1	0.3	28.9	184.9	0.6	19.3	146.8	1.1	6.3	116.4	3.0	26.6	29.3
Na^+ (mg/L)	200	3	37	1009	4.0	4	42	222	4	28	1009	3	24	803	4	13	28
SO_4^{2-} (mg/L)	250	<DL	49	263	1.3	<DL	52	263	<DL	48	255	<DL	35	230	19	29	39
Fe (mg/L)	0.3	<DL	0.11	26.16	33.6	<DL	0.10	16.20	<DL	0.11	26.16	<DL	0.24	11.13	0.02	0.06	0.37
Mn (mg/L)	0.1	<DL	0.12	7.38	53.0	<DL	0.12	2.21	<DL	0.16	7.38	<DL	0.09	2.64	0.01	0.02	0.12
NH_4^+ (mg/L)	0.64	<DL	0.04	60.00	26.8	<DL	0.08	45.00	<DL	0.03	60.00	<DL	0.02	40.00	<DL	0.02	0.02
NO_2^- (mg/L)	3.3	<DL	0.03	33.20	6.0	<DL	0.04	14.72	<DL	0.03	33.20	<DL	0.02	6.90	0.01	0.01	0.04
Pb (mg/L)	0.01	<DL	0.001	0.037	2.7	<DL	0.001	0.017	<DL	0.001	0.037	<DL	0.001	0.009	<DL	0.001	0.006
As (mg/L)	0.01	<DL	0.004	0.303	17.4	<DL	0.004	0.303	<DL	0.003	0.172	<DL	0.001	0.030	<DL	<DL	0.001
I^- (mg/L)	0.08	<DL	0.01	0.76	12.1	<DL	0.01	0.76	<DL	<DL	0.32	<DL	0.03	0.22	<DL	<DL	<DL

Note(s): AL: Allowable limits for drinking purpose in China (GAQSIQPRC, 2017); <DL: below detection limits; PAL: The proportion of samples with the concentration of one chemical above the allowable limit.

In this study, the differences in physicochemical parameter concentrations in groundwater in areas with different types of land use were investigated. As shown in Table 1, the differences of pH value in various areas were insignificant. Median values of DO and Eh in various areas were in the order of UA < PUA < AA/RA, which was opposite to the order of intensity of human activities [28]. This indicates that human activities (e.g., urbanization) result in reducing conditions in groundwater. Similarly, some redox-sensitive parameters such as Mn, NH_4^+, NO_2^-, and As, showed median values in UA and PUA higher than those in AA and RA, which was also likely attributed to the intensity of human activities in different areas. By contrast, another nitrogen compound (NO_3^-) showed median values in the order of UA > RA > PUA > AA. Groundwater TDS and most of the major ions such as Ca^{2+}, Na^+, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-} showed median values in the order of UA > PUA > AA > RA, indicating that concentrations of these components in groundwater were positively correlated with the intensity of human activities. By contrast, another major ion (K^+) showed median values in UA and AA nearly two times that in PUA and RA. The median value of groundwater Fe in AA was greater than two times that in UA and PUA and four times that in RA. This is likely ascribed to the common use of Fe-rich river water for irrigation in AA [14]. Similarly, the median value of groundwater I^- in AA was also three times or more that in other areas. Furthermore, median concentrations of groundwater Pb in various areas were the same.

As seen in Figure 3, the number of hydrochemical facies in the coastal alluvial aquifer was up to 43. Ca-HCO_3 facies was the most common hydrochemical facies (38.9%), followed by Ca·Na-HCO_3 facies (10.7%) and Ca·Na-HCO_3·Cl facies (6.7%), while others were <5%. Assuming only one major cation and one major anion remain in hydrochemical facies, the number of hydrochemical facies in the coastal alluvial aquifer was decreased to 10. The main one was also Ca-HCO_3 facies (68.5%), followed by Na-Cl facies (11.4%), Ca-Cl facies (6.7%), and Ca-NO_3 facies (5.4%), and other hydrochemical facies were <4%. Note that groundwaters with NO_3 facies accounted for 6% in the coastal alluvial aquifer; by contrast, this aquifer was free of NO_3 facies groundwater before 1980 [31]. Furthermore, groundwaters with NO_3 facies accounted for 8.7% in PUA and 8% in AA, both were two or more times that in UA, whereas the RA groundwater was free of NO_3 facies (Figure 3). These indicate that human activities resulted in the occurrence of NO_3 facies in the groundwater of this aquifer via wastewater infiltration and sewage irrigation, because sewage irrigation and wastewater infiltration were major driving forces for groundwater NO_3^- contamination in AA and PUA, respectively [11,20].

4.2. Groundwater Quality in the Coastal Alluvial Aquifer

The proportion of groundwaters with a concentration of one chemical above the allowable limit (PAL) was also shown in Table 1. In the study area, Mn showed the highest PAL of 53%, followed by Fe, NH_4^+, As, I^-, NO_3^-, TDS, NO_2^-, Cl^-, Na^+, Pb, and SO_4^{2-}, and PALs of the former six chemicals were higher than 10%. As shown in Figure 4, the groundwater quality for various groundwaters was assessed by the FSEM and classified into five classes. In this coastal alluvial aquifer, classes I, II, III, IV, and V of groundwaters accounted for 30.9%, 11.4%, 19.5%, 10.7%, and 27.5%, respectively (Figure 4). That is, 61.8% groundwaters with good quality (classes I–III) were drinkable and fit for irrigation and other purposes; 10.7% groundwaters (class IV) were undrinkable but fit for irrigation; only 27.5% groundwaters (class V) were undrinkable and unfit for other purposes. Groundwater quality was distinct in various areas. Groundwaters with poor quality (classes IV and V) in UA and AA accounted for 41.3% and 40.0%, respectively, and both were 1.1–1.2 times that in PUA; by contrast, all groundwaters in RA were drinkable (Figure 5). This indicates that human activities such as urbanization and agricultural activities deteriorated groundwater quality in the coastal alluvial aquifer [11].

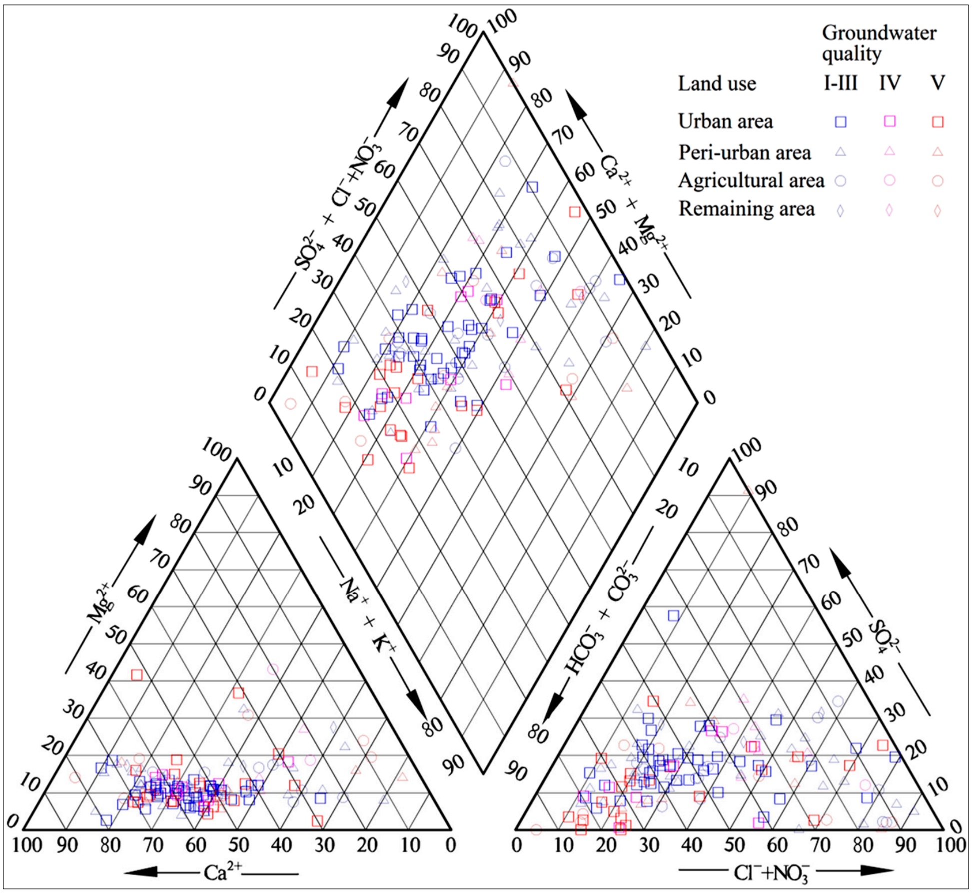


Figure 3. Hydrochemical facies of groundwater in areas with different types of land use of the coastal alluvial aquifer.

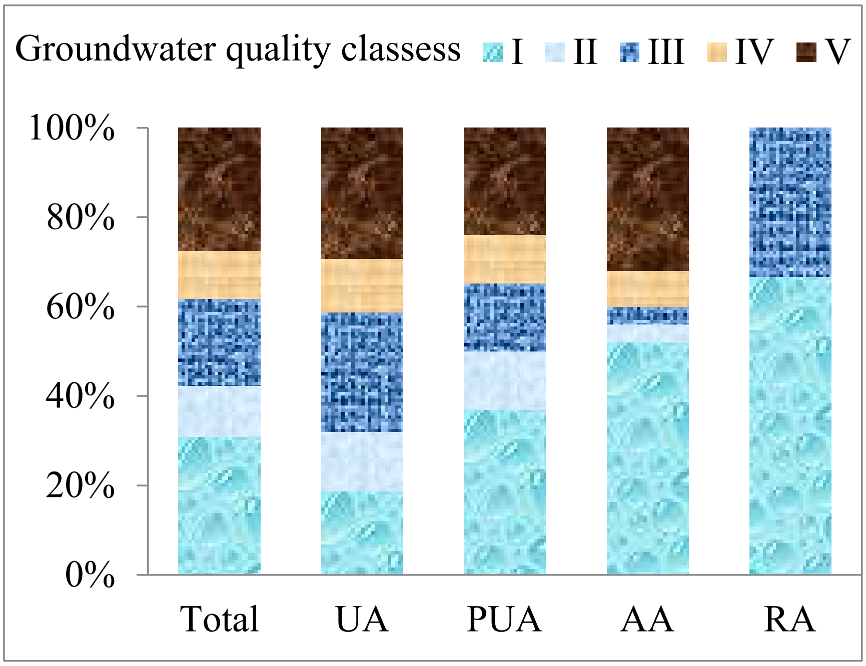


Figure 4. Groundwater quality in areas with different types of land use of the coastal alluvial aquifer.

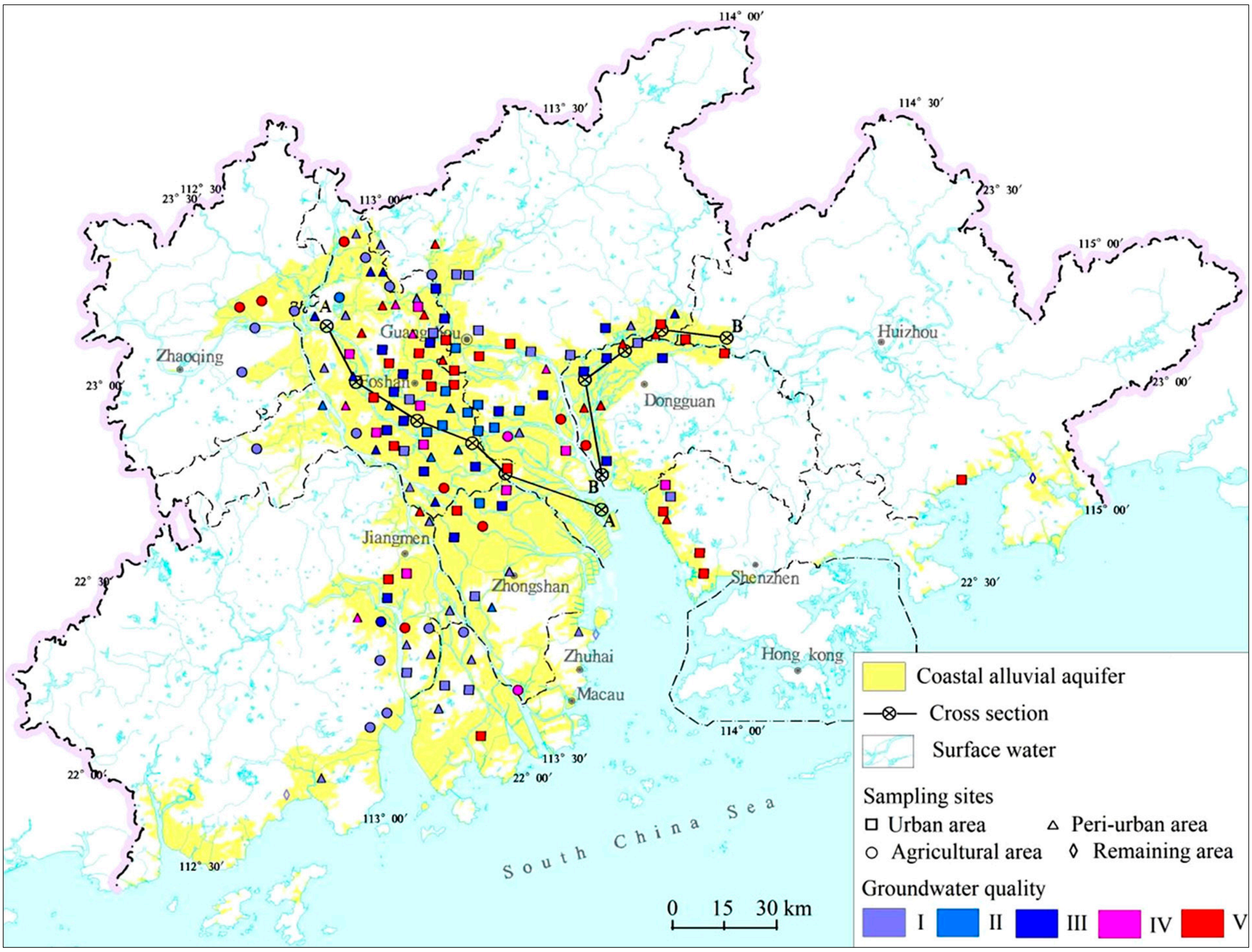


Figure 5. Spatial distribution of groundwater quality in the coastal alluvial aquifer of the Pearl River Delta.

5. Discussion

Generally, in groundwater disturbed by human activities, the PCA technique can distinguish those chemical parameters indicating anthropogenic impact from chemical parameters controlled by natural background [7,32]. In this study, five PCs were extracted by using the PCA technique, and explained 72.5% of the variance in the hydrochemical datasets of the coastal alluvial aquifer (Table 2). Specifically, the PC1, PC2, PC3, PC4, and PC5 explained 25.6%, 16.0%, 12.5%, 10.5%, and 7.8% of the total variance, respectively. Thus, factors controlling groundwater chemistry and quality in the study area are as follows.

Table 2. Principal component (PC) loadings for groundwater chemical parameters in the coastal alluvial aquifer of the Pearl River Delta.

Chemical Parameters	PCs				
	PC1	PC2	PC3	PC4	PC5
Cl^-	**0.973**	−0.005	0.072	0.050	0.017
Na^+	**0.972**	0.055	0.080	0.039	0.043
Mg^{2+}	**0.863**	0.183	0.106	0.123	−0.094

Table 2. *Cont.*

Chemical Parameters	PCs				
	PC1	**PC2**	**PC3**	**PC4**	**PC5**
TDS	**0.850**	0.488	0.079	0.092	0.082
NH_4^+	**0.622**	0.137	0.205	0.123	0.497
Ca^{2+}	0.020	**0.932**	0.030	0.074	0.021
HCO_3^-	0.304	**0.797**	−0.062	0.416	0.133
SO_4^{2-}	0.074	**0.578**	0.447	−0.404	−0.165
K^+	0.266	**0.570**	−0.085	−0.334	0.007
Pb	0.160	−0.094	**0.894**	−0.099	−0.016
Mn	0.028	0.084	**0.840**	0.181	0.094
NO_3^-	0.003	0.094	−0.078	**−0.796**	0.073
Fe	0.311	0.008	0.453	**0.472**	−0.009
As	0.220	0.177	−0.031	**0.444**	0.121
NO_2^-	0.092	0.191	0.029	−0.235	**0.768**
I^-	−0.049	−0.124	−0.013	0.176	**0.571**
Eigenvalue	4.1	2.6	2.0	1.7	1.3
Explained variance (%)	25.6	16.0	12.5	10.5	7.8
Cumulative % of variance	25.6	41.6	54.1	64.6	72.5

Note(s): Bold numbers = maximum absolute PC loading of one parameter.

5.1. PC1 (Factor 1)—Release from Marine Sediments and Infiltration of Domestic and Septic Sewage

Approximately one third of the parameters, including Cl^-, Na^+, Mg^{2+}, TDS, and NH_4^+, are in the PC1. Specifically, the PC1 shows strong positive loadings with Cl^-, Na^+, Mg^{2+}, and TDS and a moderate positive loading with NH_4^+ (Table 2). On one hand, in coastal aquifers of the PRD, co-occurrence of high levels of Cl^-, Na^+, Mg^{2+}, and TDS in groundwater was commonly from three major sources. The first is the seawater intrusion, because seawater is characterized by high concentrations of Cl^-, Na^+, Mg^{2+}, and TDS, and intrusion sometimes occurs in coastal areas of the PRD [33]. The second is the release of trapped seawater in marine sediments entering into groundwater via vertical water flow, because trapped seawater is often retained in marine sediments of Asian deltas [34]. The third is the infiltration of domestic and septic sewage, because domestic and septic sewage is generally enriched with Cl^-, Na^+, Mg^{2+}, and TDS [9], and the leakage of domestic and septic sewage often occurs in UA and PUA of the PRD [21,26]. On the other hand, seawater in the South China Sea is generally at low NH_4^+ concentrations of <0.003 mg/L and less than one tenth of the median concentration of groundwater NH_4^+ in the coastal alluvial aquifer (Table 1) [35]. This indicates that the seawater intrusion is excluded out of the PC1. By contrast, Quaternary marine sediments in the PRD are commonly enriched with organic nitrogen that converted to NH_4^+ under reducing conditions, and finally entering into groundwater via the vertical water flow [36]. This indicates that the PC1 includes the release of seawater and NH_4^+ from marine sediments. In addition, domestic and septic sewage in the PRD was also often enriched with NH_4^+ (>5 mg/L) [21], indicating that the PC1 also includes the infiltration of domestic and septic sewage. Therefore, factor 1 represents the release of salt and NH_4^+ from Quaternary marine sediments, and the infiltration of domestic and septic sewage.

5.2. PC2 (Factor 2)—Agricultural Activities

One fourth of the parameters, including Ca^{2+}, HCO_3^-, SO_4^{2-}, and K^+, are in the PC2. Specifically, the PC2 shows strong positive loadings with Ca^{2+} and HCO_3^-, and moderate positive loadings with SO_4^{2-} and K^+ (Table 2). Some studies reported that Ca-HCO_3 and Ca-SO_4 facies were two major hydrochemical facies in river water of the PRD, and irrigation using river water often occurs in agricultural lands of the PRD [21,32]. This indicates that agricultural irrigation may be included in the PC2. However, the median K^+ concentration in river water of the PRD was <10 mg/L and less than half of that in groundwater in the coastal alluvial aquifer [20], indicating that river water in the PRD was often not enriched with K^+. This seems opposite to the result that Ca^{2+}, HCO_3^-, SO_4^{2-}, and K^+ are in the same PC. On the other hand, the wide use of chemical fertilizers such as potassium fertilizers in agricultural activities often results in groundwater in agricultural lands becoming enriched with K^+ [37]. Correspondingly, in this coastal alluvial aquifer, groundwater in AA showed a much higher median K^+ concentration (22 mg/L) in comparison with that in PUA (14 mg/L) and RA (12 mg/L) (Table 1). Therefore, it can be concluded that factor 2 represents agricultural activities related to irrigation of river water and the use of chemical fertilizers.

5.3. PC3 (Factor 3)—Industrial Pollution Related to Heavy Metals and Acid Deposition

The two parameters of Pb and Mn are in the PC3. Specifically, the PC3 has strong positive loadings with Pb and Mn (Table 2). Two studies have already reported that high levels of heavy metals such as Pb and Mn in shallow groundwater of the PRD were mainly attributed to the infiltration of industrial wastewater [16,17], because illegal discharge of industrial wastewater from factories sometimes occurred in UA and PUA and irrigation using river water contaminated by industrial wastewater often occurred in AA of the PRD [32]. Correspondingly, median concentrations of groundwater Mn in UA, PUA, and AA were more than four times that in RA where industrial wastewater is free, and high Pb concentrations (>0.01 mg/L) of groundwaters occurred in UA and PUA, but not in AA and RA (Table 1). On the other hand, two studies showed that high levels of Pb in soils were widely distributed in the PRD owing to the pollution of automobile exhausts and Pb-rich industrial dusts [38,39]. Moreover, acid deposition also widely occurred in the PRD in recent decades [40]. In this case, the release of Pb from soils under acidic conditions entering into groundwater via the water flow is expected. Correspondingly, the PC3 also has a weak positive loading with SO_4^{2-} (a major chemical component in acid rain) (Table 2), and the groundwater Pb concentration had a significantly negative correlation with pH ($p < 0.001$) (Figure 6A). Therefore, it can be concluded that factor 3 represents the industrial pollution related to heavy metals and acid deposition.

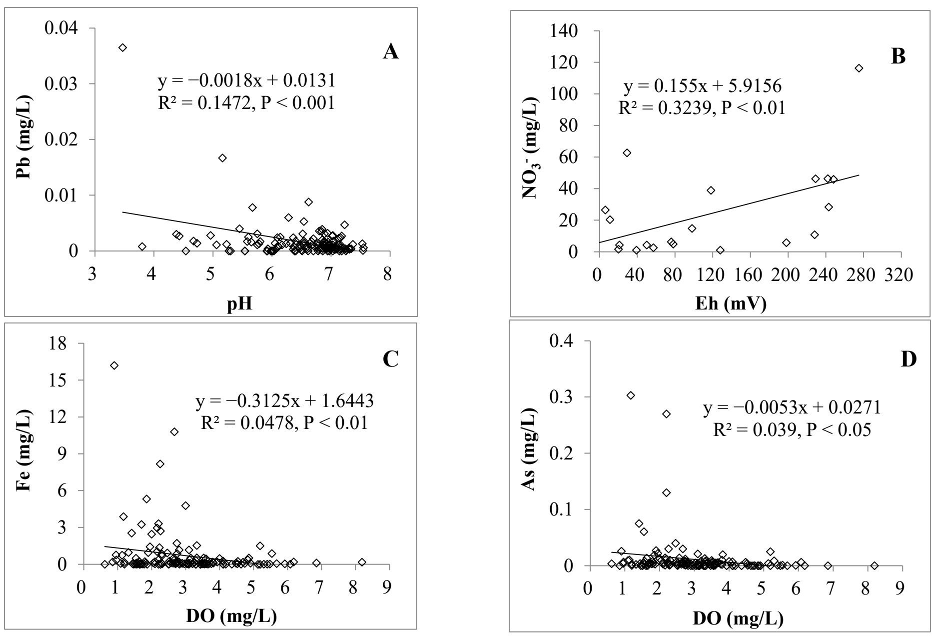


Figure 6. Relationships between concentrations of groundwater chemicals in the coastal alluvial aquifer of the Pearl River Delta. (**A**) Pb and pH; (**B**) NO_3^- and Eh in agricultural areas; (**C**) Fe and DO; (**D**) As and DO.

5.4. PC4 (Factor 4)—Reductive Dissolution of As-Loaded Fe Minerals and Denitrification

The PC4 has a strong negative loading with NO_3^- and weak positive loadings with Fe and As (Table 2). This likely infers the denitrification and the release of Fe and As via reductive dissolution, because groundwater denitrification often occurred in the PRD in 2006 [20], and reductive dissolution of As-loaded Fe minerals in Quaternary sediments induced by reducing sewage was a major driving force for the occurrence of Fe-rich and As-rich groundwaters in the PRD [14,28]. This is also supported by two evidences. One is that groundwater NO_3^- concentrations in AA had a significantly positive correlation with Eh values (Figure 6B). Another is that both Fe and As groundwater concentrations had significantly negative correlations with DO values in this coastal alluvial aquifer (Figure 6C,D). Furthermore, inputs of reducing sewage often occurred in UA, PUA, and AA of the PRD via infiltration of wastewater and irrigation with contaminated river water, respectively [14]. Thus, factor 4 likely represents the input of anthropogenic reducing sewage inducing reductive dissolution of As-loaded Fe minerals and denitrification.

5.5. PC5 (Factor 5)—I^- Contamination

The PC5 shows a strong positive loading with NO_2^- and a moderate positive loading with I^- (Table 2). This probably indicates I^- contamination from both of geogenic and anthropogenic sources, because mineralization of iodine-rich organic matter in marine sediments triggering by nitrogen-rich (e.g., NO_2^-, NH_4^+) sewage was a major geogenic source for high levels of groundwater I^- in the coastal alluvial aquifer, and the leakage of I^--rich sewage and irrigation using I^--rich and nitrogen-rich (e.g., NO_2^-, NH_4^+) river water were main anthropogenic sources for high levels of groundwater I^- in UA and AA of the coastal alluvial plain, respectively [18]. Correspondingly, median values of groundwater I^- in UA and AA were higher than that in PUA and RA (Table 1). Moreover, the PC5 also has a weak positive loading with NH_4^+ (Table 2). Therefore, factor 5 likely represents the I^- contamination from both geogenic and anthropogenic sources.

6. Conclusions

Hydrogeochemical characteristics and groundwater quality in the coastal alluvial aquifer of the PRD were investigated in this study, and were found to be dominated by Ca-HCO_3 and Ca·Na-HCO_3 facies. Groundwater with NO_3 facies occurred in this aquifer with the increase in human activities. Groundwater TDS and most of the major ion (e.g., Ca^{2+}, Na^+, Mg^{2+}, HCO_3^-, Cl^-, and SO_4^{2-}) concentrations were commonly in the order of UA > PUA > AA > RA. Redox-sensitive parameters such as Mn, NH_4^+, NO_2^-, and As in groundwater showed higher median concentrations in UA and PUA than in AA and RA. In this aquifer, 61.8% of groundwaters (classes I–III) were fit for drinking and other purposes, and 10.7% groundwaters (class IV) were undrinkable but fit for irrigation, whereas 27.5% of groundwaters (class V) were unfit for any purpose. Poor-quality groundwater in UA and AA was 1.1–1.2 times that in PUA but absent in RA.

Groundwater chemistry and quality in this aquifer was mainly controlled by five factors according to the PCA method. Factor 1 is the release of salt and NH_4^+ from marine sediments and infiltration of domestic and septic sewage. Factor 2 is agricultural activities related to the irrigation using river water and the use of chemical fertilizers. Factor 3 is the industrial pollution related to heavy metals and acid deposition. Factor 4 is the input of anthropogenic reducing sewage inducing the reductive dissolution of As-loaded Fe minerals and denitrification. Factor 5 is the I^- contamination from both geogenic and anthropogenic sources.

Correspondingly, there are three major suggestions to protect groundwater quality in this coastal aquifer. (1) Repairing old sewer systems in UA and building sewer systems in PUA to reduce illegal discharge of sewage. (2) Limiting sewage irrigation and the use of chemical fertilizers in AA. (3) Strengthening the supervision of the industrial exhaust gas discharge in UA and PUA.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14244131/s1, Table S1: Groundwater quality standards for drinking and irrigation [22]; Table S2: Kaiser-Meyer-Olkin and Bartlett's test for the suitability of principal components analysis (PCA) to groundwater chemical data in coastal alluvial aquifer.

Author Contributions: Conceptualization, C.L.; methodology, C.L. and Q.H.; software, Y.C.; validation, C.L. and G.H.; investigation, C.L. and G.H.; data curation, Q.H.; writing—original draft preparation, C.L.; writing—review and editing, Q.H. and G.H.; visualization, Q.H.; supervision, G.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Natural Science Foundation of Hebei Province, China (D2021504031), the Three-three-three Talent Project of Hebei Province, China (A202105001), and the China Geological Survey Grant (DD20160309).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets generated and/or analyzed during the current study are not publicly available.

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

References

1. Huang, G.; Liu, C.; Sun, J.; Zhang, M.; Jing, J.; Li, L. A regional scale investigation on factors controlling the groundwater chemistry of various aquifers in a rapidly urbanized area: A case study of the Pearl River Delta. *Sci. Total Environ.* **2018**, *625*, 510–518. [CrossRef] [PubMed]
2. Liu, X.; Xin, L. Assessment of the efficiency of cultivated land occupied by urban and rural construction land in China from 1990 to 2020. *Land* **2022**, *11*, 941. [CrossRef]
3. Small, C.; Nicholls, R.J. A global analysis of human settlement in coastal zones. *J. Coast. Res.* **2003**, *19*, 584–599.
4. Umarani, P.; Ramu, A.; Kumar, V. Hydrochemical and statistical evaluation of groundwater quality in coastal aquifers in Tamil Nadu, India. *Environ. Earth Sci.* **2019**, *78*, 452. [CrossRef]
5. Chucuya, S.; Vera, A.; Pino-Vargas, E.; Steenken, A.; Mahlknecht, J.; Montalván, I. Hydrogeochemical characterization and identification of factors influencing groundwater quality in coastal aquifers, case: La Yarada, Tacna, Peru. *Int. J. Environ. Res. Public Health* **2022**, *19*, 2815. [CrossRef]
6. Armengol, S.; Ayora, C.; Manzano, M.; Bea, S.A.; Martínez, S. The role of loess weathering in the groundwater chemistry of the Chaco-Pampean Plain (Argentina). *J. Hydrol.* **2020**, *587*, 124984. [CrossRef]
7. Kanellopoulos, C.; Argyraki, A. Multivariate statistical assessment of groundwater in cases with ultramafic rocks and anthropogenic activities influence. *Appl. Geochem.* **2022**, *141*, 105292. [CrossRef]
8. Mason, J.P. *Groundwater, Surface-Water, and Water-Chemistry Data, Black Mesa Area, northeastern Arizona—2018–2019. U.S. Geological Survey Open-File Report*; 2022–1086; USGS: Reston, VI, USA, 2022. [CrossRef]
9. Elumalai, V.; Rajmohan, N.; Sithole, B.; Li, P.; Uthandi, S.; Tol, J. Geochemical evolution and the processes controlling groundwater chemistry using ionic ratios, geochemical modelling and chemometric analysis in uMhlathuze catchment, KwaZulu-Natal, South Africa. *Chemosphere* **2023**, *312*, 137179. [CrossRef]
10. Han, D.; Currell, M.J. Review of drivers and threats to coastal groundwater quality in China. *Sci. Total Environ.* **2022**, *806*, 150913. [CrossRef]
11. Sellamuthu, S.; Joseph, S.; Gopalakrishnan, S.; Sekar, S.; Khan, R.; Shukla, S. Appraisal of groundwater quality for drinking and irrigation suitability using multivariate statistical approach in a rapidly developing urban area, Tirunelveli, India. *Environ. Sci. Pollut. Res.* **2022**. [CrossRef]
12. Xing, L.; Guo, H.; Zhan, Y. Groundwater hydrochemical characteristics and processes along flow paths in the North China Plain. *J. Asian Earth Sci.* **2013**, *70–71*, 250–264. [CrossRef]
13. Ri, M.; Guo, H.; Kim, P.; Ri, K.; Ri, G. Influence of seawater intrusion on the hot springs in a coastal area: The case of the Anak-Sinchon Uplift, Korean Peninsula. *J. Hydrol.* **2022**, *607*, 127509. [CrossRef]
14. Huang, G.; Han, D.; Song, J.; Li, L.; Pei, L. A sharp contrasting occurrence of iron-rich groundwater in the Pearl River Delta during the past dozen years (2006–2018): The genesis and mitigation effect. *Sci. Total Environ.* **2022**, *829*, 154676. [CrossRef] [PubMed]
15. Huang, G.; Zhang, M.; Liu, C.; Li, L.; Chen, Z. Heavy metal(loid)s and organic contaminants in groundwater in the Pearl River Delta that has undergone three decades of urbanization and industrialization: Distributions, sources, and driving forces. *Sci. Total Environ.* **2018**, *635*, 913–925. [CrossRef]
16. Zhang, F.; Huang, G.; Hou, Q.; Liu, C.; Zhang, Y.; Zhang, Q. Groundwater quality in the Pearl River Delta after the rapid expansion of industrialization and urbanization: Distributions, main impact indicators, and driving forces. *J. Hydrol.* **2019**, *577*, 124004. [CrossRef]

17. Hou, Q.; Zhang, Q.; Huang, G.; Liu, C.; Zhang, Y. Elevated manganese concentrations in shallow groundwater of various aquifers in a rapidly urbanized delta, south China. *Sci. Total Environ.* **2020**, *701*, 134777. [CrossRef]
18. Huang, G.; Liu, C.; Li, L.; Zhang, F.; Chen, Z. Spatial distribution and origin of shallow groundwater iodide in a rapidly urbanized delta: A case study of the Pearl River Delta. *J. Hydrol.* **2020**, *585*, 124860. [CrossRef]
19. Huang, G.; Liu, C.; Zhang, Y.; Chen, Z. Groundwater is important for the geochemical cycling of phosphorus in rapidly urbanized areas: A case study in the Pearl River Delta. *Environ. Pollut.* **2020**, *260*, 114079. [CrossRef]
20. Zhang, M.; Huang, G.; Liu, C.; Zhang, Y.; Chen, Z.; Wang, J. Distributions and origins of nitrate, nitrite, and ammonium in various aquifers in an urbanized coastal area, south China. *J. Hydrol.* **2020**, *582*, 124528. [CrossRef]
21. Sun, J.; Jing, J.; Huang, G.; Liu, J.; Chen, X.; Zhang, Y. *Report on the Investigation and Assessment of Groundwater Contamination in the Pearl River Delta Area*; Chinese Academy of Geological Sciences; The Institute of Hydrogeology and Environmental Geology: Beijing, China, 2009. (In Chinese)
22. General Administration of Quality Supervision Inspection and Quarantine of the People's Republic of China (GAQSIQPRC). *Standard for Groundwater Quality*; Standards Press of China: Beijing, China, 2017.
23. Bi, P.; Huang, G.; Liu, C.; Li, L. Geochemical factors controlling natural background levels of phosphate in various groundwater units in a large-scale urbanized area. *J. Hydrol.* **2022**, *608*, 127594. [CrossRef]
24. Zong, Y.; Yim, W.W.S.; Yu, F.; Huang, G. Late Quaternary environmental changes in the Pearl River mouth region, China. *Quat. Int.* **2009**, *206*, 35–45. [CrossRef]
25. Lancia, M.; Su, H.; Tian, Y.; Xu, J.; Andrews, C.; Lerner, D.N.; Zheng, C. Hydrogeology of the Pearl River Delta, southern China. *J. Maps* **2020**, *16*, 388–395. [CrossRef]
26. Huang, G.; Pei, L.; Li, L.; Liu, C. Natural background levels in groundwater in the Pearl River Delta after the rapid expansion of urbanization: A new pre-selection method. *Sci. Total Environ.* **2022**, *813*, 151890. [CrossRef]
27. Ye, Y.; Zhang, H.; Liu, K.; Wu, Q. Research on the influence of site factors on the expansion of construction land in the Pearl River Delta, China: By using GIS and remote sensing. *Int. J. Appl. Earth Obs.* **2013**, *21*, 366–373. [CrossRef]
28. Huang, G.; Song, J.; Han, D.; Liu, R.; Liu, C.; Hou, Q. Assessing natural background levels of geogenic contaminants in groundwater of an urbanized delta through removal of groundwaters impacted by anthropogenic inputs: New insights into driving factors. *Sci. Total Environ.* **2023**, *857*, 159527. [CrossRef]
29. Huang, G.; Chen, Z.; Liu, F.; Sun, J.; Wang, J. Impact of human activity and natural processes on groundwater arsenic in an urbanized area (South China) using multivariate statistical techniques. *Environ. Sci. Pollut. R.* **2014**, *21*, 13043–13054. [CrossRef]
30. Güler, C.; Kurt, M.A.; Alpaslan, M.; Akbulut, C. Assessment of the impact of anthropogenic activities on the groundwater hydrology and chemistry in Tarsus coastal plain (Mersin, SE Turkey) using fuzzy clustering, multivariate statistics and GIS techniques. *J. Hydrol.* **2012**, *414–415*, 435–451. [CrossRef]
31. Guangdong Hydrogeological Second Team (GHST). *Regional Hydrogeological Survey Report*; Guangdong Hydrogeological Second Team: Guangzhou, China, 1981. (In Chinese)
32. Huang, G.; Sun, J.; Zhang, Y.; Chen, Z.; Liu, F. Impact of anthropogenic and natural processes on the evolution of groundwater chemistry in a rapidly urbanized coastal area, South China. *Sci. Total Environ.* **2013**, *463–464*, 209–221. [CrossRef]
33. Wang, Y.; Jiao, J.J. Origin of groundwater salinity and hydrogeochemical processes in the confined Quaternary aquifer of the Pearl River Delta, China. *J. Hydrol.* **2012**, *438–439*, 112–124. [CrossRef]
34. Larsen, F.; Tran, L.V.; Van Hoang, H.; Tran, L.T.; Christiansen, A.V.; Pham, N.Q. Groundwater salinity influenced by Holocene seawater trapped in incised valleys in the Red River delta plain. *Nat. Geosci.* **2017**, *10*, 376–381. [CrossRef]
35. Zhu, Y.; Yuan, D.; Huang, Y.; Ma, J.; Feng, S. A sensitive flow-batch system for on board determination of ultra-trace ammonium in seawater: Method development and shipboard application. *Anal. Chim. Acta* **2013**, *794*, 47–54. [CrossRef] [PubMed]
36. Jiao, J.; Wang, Y.; Cherry, J.A.; Wang, X.; Zhi, B.; Du, H.; Wen, D. Abnormally high ammonium of natural origin in a coastal aquifer-aquitard system in the Pearl River Delta, China. *Environ. Sci. Technol.* **2010**, *44*, 7470–7475. [CrossRef] [PubMed]
37. Shamrukh, M.; Corapcioglu, M.Y.; Hassona, F.A.A. Modeling the Effect of Chemical Fertilizers on Ground Water Quality in the Nile Valley Aquifer, Egypt. *Groundwater* **2001**, *39*, 59–67. [CrossRef]
38. Zhu, B.; Chen, Y.; Peng, J. Lead isotope geochemistry of the urban environment in the Pearl River Delta. *Appl. Geochem.* **2001**, *16*, 409–417.
39. Yin, G.; Zhu, H.; Chen, Z.; Su, C.; He, Z.; Chen, X.; Qiu, J.; Wang, T. Spatial distribution and source apportionment of soil heavy metals in Pearl River Delta, China. *Sustainability* **2021**, *13*, 9651. [CrossRef]
40. Liu, F.; Sun, J.; Wang, J.; Zhang, Y. Groundwater acidification in shallow aquifers in Pearl River Delta, China: Distribution, factors, and effects. *Geochem. J.* **2017**, *51*, 373–384. [CrossRef]