Research Article

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Natural and human-induced factors controlling the phreatic groundwater geochemistry of the Longgang River basin, South China

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Abstract: Groundwater chemical evolution is the key to ensuring the sustainability of local society and economy development. In this study, four river sections and 59 groundwater wells are investigated in the Longgang River (L.R.) basin in South China. Comprehensive hydrochemical analysis methods are adopted to determine the dominant factors controlling the chemical evolution of the local phreatic groundwater and the potential impact of human activities on groundwater quality. The results indicate that the ionic composition of the local phreatic groundwater is dominated by Ca^{2+} (0.9–93.8 mg/L), HCO_3^- (4.4–280.0 mg/L), and SO_4^{2-} (1.0–91.0 mg/L). Ca-Mg-HCO_3 , Ca-Na-HCO_3 , and Na-Ca-HCO_3 are the major groundwater hydrochemical facies. Water–rock interactions, such as the dissolution of calcite and dolomite, are the primary source of the major ions in the local groundwater. Cation-exchange reaction has its effects on the contents of Ca^{2+} , Mg^{2+} , and Na^+ . Ammonia concentration of the sampling sections in the L.R. increases from 0.03 to 2.01 mg/L along the flow direction. Groundwater nitrate in the regions of the farmland is attributed to the lowest level of the

groundwater quality standards of China, while the same test results are obtained for heavy metals in the industrial park and landfill, suggesting a negative impact of the anthropogenic activities on the local phreatic groundwater quality.

Keywords: groundwater, geochemistry, anthropogenic activities, pollution, conceptual model

1 Introduction

Groundwater is the most important source of freshwater throughout the world, and one-third of the world's population relies on groundwater supply [1–3]. Unfortunately, rapid urbanization and increasing population have accelerated the consumption of groundwater resources and caused deterioration in groundwater quality [4–6], which raises concern about the drinking water safety worldwide, especially in the developing countries such as India, Pakistan, and China [7–9]. Therefore, understanding the chemical composition of groundwater will aid in the development and management of groundwater for various uses [6,10,11].

Groundwater chemical evolution is largely dominated by the natural factors (topography and landforms, stratum, lithology, meteorological conditions, water–rock interaction, etc.) and the anthropogenic activities (agricultural irrigation, exploitation for domestic water supply and industrial manufacturing, etc.) [12–14]. A significant number of studies have been conducted on this topic owing to the importance of the domestic water supply. For instance, studies focused on the anthropogenic activities resulting in groundwater pollution of nitrate/heavy metals [15–21]; groundwater geochemical assessment using geostatistical and geographic information system approaches [22–24]; and groundwater salinization related to pumping and irrigation [25,26]. However, the regions with highly developed river net (such as the South China) generally consider the surface

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water (the rivers and the reservoirs) as the domestic water supply source; thus, the prevention of surface water pollution in such regions is emphasized, while the attention paid to the groundwater is not enough [27,28]. For instance, Shenzhen, considered one of the most developed cities in China (1,997 km², 12.5 million population, and GDP 2.24 trillion CNY in 2017) [29], did not conduct the basic status survey of the groundwater quality until 2013 [30], and the research focused on groundwater chemical evolution in basin scale has not yet been reported. Despite the importance of the groundwater resource, groundwater hydrological information and the geochemical behavior of the groundwater system are of great significance to assess the groundwater sustainability as well as local water environment [31–35]. So it is necessary to identify the dominant factors that control the groundwater chemical evolution in such regions.

In the context of current needs, geochemical survey was conducted in the L.R. basin in Shenzhen, South China, and the specific objectives of this study were to (1) investigate the geochemical evolution of groundwater in the L.R. basin using the hydrochemical analysis methods; (2) evaluate the local water quality status and the predominant factors of natural and anthropogenic activities on the groundwater chemistry; and (3) identify the impact of the potential pollution sources on the groundwater quality. Taking the L.R. basin as an example, the results of this study partly reveal the negative impacts of urbanization on the local water quality and groundwater chemical evolution, which will be beneficial to promote the groundwater management for sustainable development in such rapidly urbanizing areas.

2 Study area description

The L.R. basin is located in the northeastern region of Shenzhen, South China, extending between 22°34'N to 22°49'N latitude and 114°09'E to 114°26'E longitude (Figure 1), the area and population of which are c. 302 km² and 1.18 million, respectively. The Shenzhen Water Resources Bulletin 2017 indicates that the total water consumption of the L.R. basin is c. $27,367 \times 10^4$ m³ and the consumption of groundwater is c. 65×10^4 m³ [36]. The climate of the study area is typically subtropical monsoon, with the average monthly temperature varying from 15.4°C in January to 28.9°C in July (1981–2010) [37]. According to the meteorological

data collected at the Qinglinjing Weather Station from 1960 to 1997, the average annual precipitation of the L.R. basin is c. 1,733.8 mm, ranging from 979 to 2,467 mm, and approximately 80% of the precipitation occurs during April and September [37]. The length and the river bed gradient is c. 36.3 km and 2.8‰, with 11 first tributaries distributed in arborescent pattern, and the flow direction is roughly from southwest to northeast.

The NE–SW Lianhuashan Fault Zone and E–W Gaoyao–Huilai fault zone dominate the geological process of the L.R. basin, and the stratum of the study area mainly consists of sediments and igneous rocks, such as the quaternary sediments that distribute in the middle of the basin and the carboniferous sandstones that distribute in the northeast and the southern basin (Figure 2a). The hydrogeological division of the L.R. basin is complex owing to the strong geological activities; quaternary sediments are mainly distributed in the middle part of the basin, while carboniferous sandstones are distributed in the west and south of the middle part. Silurian granites, cretaceous sandstones, and conglomerates are distributed in the north and south of the basin in a scattered manner. Precipitation is the major recharge source of the local phreatic groundwater, which is exploited for the needs of distributed agricultural irrigation, industrial manufacturing, and domestic use in the study area. According to the boreholes work conducted in 2014 and 2015, the phreatic groundwater in the study area mainly flows from northeast to southwest, the aquifer of which is composed of variable materials such as silt clay, sandy clay, and weathered granite, and the thickness of the phreatic aquifer ranges from 2.6 to 6.8 m, with the water table depth varying from 1.0 to 6.8 m (Figure 2b and c).

3 Materials and methods

To reveal the hydrogeochemical characteristics, rainwater, river water, and groundwater were sampled in the L.R. basin in 2015. In this study, a total of 59 groundwater samples were collected from different sampling sites (12 wells in the farmland for agricultural supply and 47 wells in the construction land for domestic use and groundwater quality monitoring, Figure 1). The selection of sampling locations was based on the field conditions and followed the technical specifications for environmental monitoring of groundwater of China [38].

Figure 1: Geographical location of the L.R. basin.

The river samples were collected from four river sections once per month (numbered from 1 to 4, from the upstream to the downstream), and the rainwater samples were collected from the Longgang Weather Monitoring Station. The river water and groundwater samples were collected using high-density polyethylene containers and transported to the State Environmental Protection Key Laboratory of Drinking Water Source Management and Technology (Shenzhen) for test. The sampling number and frequency, the test parameters, and the methods used are summarized in Table 1. Test procedures followed the standard examination methods for drinking water of China [39]. Ion balance check was conducted to assess the reliability of the hydrochemical data; 72% (18/25) of the calculated charge balance errors of the samples were found to be less than $\pm 10\%$ (44% were less than 5%), which was an acceptable uncertainty for the hydrochemical analysis in this study. (Seven samples with charge balance errors larger than 10% were excluded from the hydrogeochemical analysis.)

4 Results and discussion

4.1 General hydrochemistry

The statistical values of pH, dissolved oxygen (DO), electric potential (Eh), electrical conductivity (EC), total dissolved solid (TDS) of the local phreatic groundwater are shown in Figure 3a. According to the test results, the pH and DO range from 3.95 (outlier) to 7.76 and from 1.75 to 8.85 mg/L, respectively, with the average value of 6.55 and 5.13 mg/L, indicating slightly acidic and aerobic conditions of the local phreatic groundwater. The TDS ranges from 16 to 2,070 mg/L (outlier), and the average value is 380 mg/L; the Eh and EC range from 280 to 729 mV and from 42.7 to 944.0 $\mu\text{S}/\text{cm}$, respectively. The outliers of the pH and TDS are attributed to the grade 5 of the standard of groundwater quality (on a scale of one to five to measure the quality of groundwater, one means good and five means poor [40]), indicating that the phreatic groundwater in some regions of the study area is of poor quality and is not potable.

Figure 2: Geological map (a) and borehole profile of the L.R. basin (b and c).

4.2 Hydrochemical facies

The ionic composition of the phreatic groundwater of the study area is dominated by Ca^{2+} (0.9–93.8 mg/L, average value 29.4 mg/L), HCO_3^- (4.4–280.0 mg/L, average value 89.9 mg/L), and SO_4^{2-} (1.0–91.0 mg/L, average value 22.9 mg/L); the concentrations of Na^+ (2.0–37.9 mg/L,

average value 10.5 mg/L), K^+ (0.3–10.7 mg/L, average value 2.8 mg/L), Mg^{2+} (0.2–14.8 mg/L, average value 4.8 mg/L), and Cl^- (2.0–47.9 mg/L, average value 16.5 mg/L) are relatively low (Figure 3b). The geochemical evolution of groundwater can be identified by plotting the concentrations of major cations and anions in the Piper trilinear diagram [41]. According to the

Table 1: Sampling and test information in this study

Cluster	Number of the sampling sites	Sampling frequency	Number of the samples	Test parameters	Number of the tested samples	Test method and instruments
Rainwater	1	1/month	12	pH, EC, ammonia	12	Electrode method (PB-10, China) for pH; electrical conductivity meter (DDS-307W, China) for EC; spectrophotometer (Hach DR1900, USA) for ammonia
River water	4	1/month	48	pH, DO, EC, Eh, TDS	48	On-site portable instrument (YSIproplus, USA)
				Ammonia	48	Spectrophotometer (Hach DR1900, USA) for ammonia
Groundwater	59	1/year	59	pH, DO, EC, Eh, TDS	59	On-site portable instrument (YSIproplus, USA)
				Na, K, Ca, Mg, Cl, SO ₄ , HCO ₃	25 (12 wells in the farmland and 13 in the construction land)	Inductively coupled plasma atomic emission spectrometry (Integra XL, GBC, Australia) for Na, K, Ca, Mg; ion chromatography (IC-90, Dinox, USA) for Cl, SO ₄ , HCO ₃ ; acid-base titration for HCO ₃
				Ammonia, nitrate, fluoride, Pb, Hg, Zn, Cu, Cd, Ni	59	Spectrophotometer (Hach DR1900, USA) for ammonia, nitrate, fluoride; inductively coupled plasma atomic emission spectrometry (Integra XL, GBC, Australia) for Pb, Hg, Zn, Cu, Cd, and Ni

Figure 3: Field monitoring parameters (a) and the major component concentration (b) of the phreatic groundwater in the study area.

distribution of the points in the plots (Figure 4), there is no obvious variance in groundwater types between the samples collected from the wells in the farmland and the construction land. Overall, 94% of the (17/18) samples are lumped in the zones A and D of the lower left triangle, indicating that calcium type and sodium type dominate the groundwater type of the study area. About

half of the samples are located in the zone E of the lower right triangle, 17% (3/18) of the samples are located in the zone B, and the rest are located in the zones F and G, which reveals that bicarbonate type groundwater and non-type groundwater are predominant and the rest are sulfate type and chloride type. Meanwhile, c. 55% (10/18) of the samples are distributed in the zone 5, indicating

Figure 4: Piper plots of the phreatic groundwater of the study area.

that the bicarbonate type is most common in groundwater chemistry of the phreatic aquifer in the study area. Therefore, the hydrochemical facies in the phreatic groundwater of the study area can be classified into a variety of water types including Ca–Mg–HCO₃, Ca–Na–HCO₃, Na–Ca–HCO₃, Na–HCO₃, and Na–SO₄–Cl types.

4.3 Natural factors affecting groundwater chemistry

The geochemical evolution of groundwater is largely determined by natural factors such as the lithology, the stratum structure, and the hydrogeological conditions [23,34,35]; thus, the water–rock interactions would probably dominate the ionic components in groundwater. The Gibbs diagram and Gaillardet diagram are intuitional tools being widely used to discuss the origin of groundwater ions and the dominant factors that control the components of groundwater [34,42–45]. According to the study results illustrated in Figure 5, the plots of the samples are mainly distributed in the middle part of the diagram (the rock dominance zone), indicating that the rock weathering (water–rock interaction) controls the chemical evolution of the local phreatic groundwater. Most of the plots are lumped in the diagram with Na⁺/(Na⁺ + Ca²⁺) ranging from 0.1 to

0.5 (Figure 5a) and Cl[−]/(Cl[−] + HCO₃[−]) ranging from 0.1 to 0.6 (Figure 5b), indicating that Ca⁺ and HCO₃[−] are the predominant components of the phreatic groundwater in the study area. The plots of the samples collected from the farmland are distributed in the relatively upper part of the diagram than those of the samples collected from the construction land, suggesting higher TDS of the phreatic groundwater in the farmland. Evaporation is a vital factor controlling the chemical evolution of phreatic groundwater [13,14]. The transpiration of the crops may result in a larger evaporation discharge in the farmland than in the construction land. Besides, groundwater abstraction and irrigation in the farmland may accelerate the groundwater flow and the dissolution of the soil/aquifer minerals, leading to a relatively higher phreatic groundwater TDS in the farmland.

Moreover, the dominant factors of groundwater chemistry can be revealed by the ratios of the milligram equivalent concentration of major components (abbreviated as r_X). For instance, the r_{Na}/r_{Cl} of seawater is *c.* 0.85–0.87; the r_{Na}/r_{Cl} of groundwater predominated by the dissolution of halite is *c.* 1; and the r_{Na}/r_{Cl} of groundwater affected by the precipitation or strong water–rock interactions (and cation exchange) is probably larger than 1 or smaller than 0.85, respectively [46]. The r_{Na}/r_{Cl} of the phreatic groundwater samples in this study ranges from 0.59 to 3.77, with an average value of 1.21 (Figure 6a), indicating that the major components of the local groundwater are probably dominated by

Figure 5: (a and b) Gibbs diagram of the phreatic groundwater of the study area.

Figure 6: (a and b) Statistical results of the milligram equivalent concentration of Na^+ , SO_4^{2-} vs Cl^- .

multiple interactions; besides, the average r_{Na^+}/r_{Cl^-} of the samples collected from the construction land is 1.48, indicating that the groundwater evolution of the construction land is probably predominated by water-rock interactions and precipitation, and it is in agreement with the results revealed by the Gibbs diagram. The $r_{SO_4^{2-}}/r_{Cl^-}$ ranges from 12.03 to 200.30, with an average value of 84.06 (Figure 6b), indicating a relative oxidation condition of the phreatic groundwater.

According to the study on the dissolved loads of 60 world's largest rivers, a calculated model based on the Na^+ normalized molar ratios was proposed by Gaillardet et al. [44,45] to discuss the possible origin of the river major component by the data plots on three end-members: weathering of evaporites, silicates, and carbonates. In Figure 7, the plots of the phreatic groundwater samples in this study are mainly distributed on the diagonal of the Gaillardet diagram. Most of the plots of the samples collected from the construction land are lumped between the silicates weathering zone and the evaporites zone, while the plots of the farmland are located toward the zone between silicates and carbonates weathering, indicating that silicates weathering and combined reactions would control the local groundwater major component.

As mentioned in Section 2, the phreatic aquifer of the study area is composed of the sediments such as quartz, calcite, dolomite, albite, halite, and gypsum; therefore, the dissolution of these minerals can be a possible source of the major groundwater ions; moreover, the possible interactions can be revealed by the

milligram equivalent concentration of the major ions in the local phreatic groundwater, and the interactions are summarized as equations (1)–(7). Equations (1) and (2) represent the dissolution of albite and calcicase, which may probably be the source of the local phreatic

Figure 7: Gaillardet diagram of the phreatic groundwater of the study area.

groundwater major components. Theoretically, if the major ions of groundwater originate from the weathering of carbonates (dissolution of calcite and dolomite [equations (3) and (4)]) or dissolution of evaporites (such as halite [equation (5)]), the $r_{\text{Ca}^{2+}} + r_{\text{Mg}^{2+}}$ vs $r_{\text{HCO}_3^-}$ and r_{Na^+} vs r_{Cl^-} should be equal to 1:1 [47–49]. In Figure 8a, the plots are distributed toward the coordinate axis of $r_{\text{Ca}^{2+}} + r_{\text{Mg}^{2+}}$, especially for the farmland samples, while in Figure 8b, most of the plots deflect from the 1:1 line, indicating the weathering of carbonates and evaporites is not the predominant factor that controls the local phreatic groundwater chemistry. The ratios of $r_{\text{Ca}^{2+}} + r_{\text{Mg}^{2+}}$ vs $r_{\text{SO}_4^{2-}} + r_{\text{HCO}_3^-}$ and $r_{\text{Ca}^{2+}}$ vs $r_{\text{SO}_4^{2-}}$ reflect whether the major components of the local groundwater originate from the dissolution of calcite, dolomite, and gypsum (if so, the samples plots should be distributed along the 1:1 line, equation (6)), while in Figure 8c and d, the opposite results are observed, suggesting relatively abundant Ca^{2+} and Mg^{2+} in the local groundwater and that there may exist other sources

for these ions [50,51]. A possible interpretation is that the sulfur and sulfide in the aquifer may be oxidized into sulfuric acid in the relatively redox condition of the local groundwater, and the calcium and magnesium minerals are dissolved with sulfuric acid (equation (7)). Besides, the groundwater content of Ca^{2+} , Mg^{2+} , and Na^+ may be affected by cation-exchange reaction, and the distribution of the ratio of $[(r_{\text{Na}^+} + r_{\text{K}^+}) - r_{\text{Cl}^-}]$ and $[(r_{\text{Ca}^{2+}} + r_{\text{Mg}^{2+}}) - (r_{\text{HCO}_3^-} + r_{\text{SO}_4^{2-}})]$ should be linear with a slope close to -1 [52,53]. In Figure 9a, the slope of the fitting line is -1.03 , which indicates that the cation-exchange reaction may have significant influence on the local phreatic groundwater chemistry. Moreover, the chloro-alkaline indices (CAI) proposed by Schoeller [54,55] are widely used to discuss the possible interactions between Ca^{2+} and Na^+ . The two indices CAI-I and CAI-II are defined as $[r_{\text{Cl}^-} - (r_{\text{Na}^+} + r_{\text{K}^+})]/r_{\text{Cl}^-}$ and $[r_{\text{Cl}^-} - (r_{\text{Na}^+} + r_{\text{K}^+})]/[r_{\text{HCO}_3^-} + r_{\text{SO}_4^{2-}} + r_{\text{CO}_3^{2-}} + r_{\text{NO}_3^-}]$, and the positive/negative values of CAI-I and CAI-II indicate that the cation-exchange reaction follows equation

Figure 8: (a–d) Scatterplots of the milligram equivalent concentration of the major ions in the local phreatic groundwater.

Figure 9: (a) The cation-exchange line and (b) the CAI of the local phreatic groundwater.

(8) or (9), respectively. As revealed by Figure 9b, most of the plots of the groundwater samples collected from the farmland are lumped on the positive zone (equation (8)), while the others are on the negative zone, suggesting that different cation-exchange reactions affect the local groundwater chemistry, and Ca minerals exchanged by Na⁺ may be a possible reason to explain the relatively abundant Ca²⁺ in the groundwater of the farmland.

4.4 Anthropogenic activities affecting groundwater chemistry

The L.R. basin is highly developed with c. 301 km² land supporting nearly 1.18 million populations [37]. According to the remote sensing image interpretation data of the basin in 2014 [37], the construction land occupies c. 44% of the whole area of the basin, while the farmland occupies c. 14%; thus, the anthropogenic activities, for instance, the exploitation of groundwater for irrigation/domestic use and the pollution caused by industrial manufacturing and production, may affect local water environment. The river sampling results indicate that ammonia, considered the most common water pollutant indicator caused by anthropogenic activities such as the sewage discharge [56–58], is the major pollutant in the L.R., and its average concentration of river sections 1–4 increases from 0.03 to 1.12, 1.31, and 2.01 mg/L (Figure 10a) along the river flow direction, suggesting the anthropogenic pollution tendency of the L.R. Meanwhile, the concentration of ammonia in the phreatic groundwater of the study area ranges from 0.01 mg/L (nine samples lower than the detection limit) to 14.20 mg/L;

Figure 10: The groundwater test results of ammonia (a), nitrate (b), Hg, Cd, Cu (c), and Ni, Zn, Pb (d) of the study area (the white, orange, and red dots in Figure 10(a) and (b) indicate the test results under the standard of the groundwater quality of P. R. China [40] for Level-3, Level-4, and Level-5, respectively).

28.8% (17 of 59) of the samples are attributed to the lowest level of the standard for groundwater quality of

P. R. China [40] (Level-5, ammonia-N; Table 2), 14 of which were sampled from the construction land (Figure 10a),

Table 2: The environment quality standards for surface water and the standard for groundwater quality of P. R. China (ammonia, nitrate, Ni, and Pb) [40,63]

Standards	Surface water (GB 3838-2002)	Chemicals (mg/L)				
		Category/uses		Chemicals (mg/L)		
				Ammonia	Nitrate	Pb
Level-1	Headstream water; National Nature Reserve			≤0.15	≤10 (surface water source protection zone of the centralized drinking water sources)	≤0.01 (surface water source protection zone of the centralized drinking water sources)
Level-2	Surface water source protection zone 1 of the centralized drinking water sources; cherish aquatic habitats, spawning grounds of fishes and shrimps, feeding grounds of the larva fishes, etc.			≤0.5		≤0.01
Level-3	Surface water source protection zone 2 of the centralized drinking water sources; wintering grounds and migration channels of fishes and shrimps, aquaculture area, swimming area, etc.			≤1		≤0.05
Level-4	General industrial water area; recreational water area that is not directly in contact with the human body			≤1.5		≤0.05
Level-5	Agricultural water area; general landscape requirement water area			≤2.0		≤0.1

Standards	Groundwater (GB 14848-2017)	Chemicals (mg/L)				
		Category/uses		Chemicals (mg/L)		
				Ammonia	Nitrate	Pb
Level-1	Various uses			≤0.02	≤2	≤0.002
Level-2	Various uses			≤0.1	≤5	≤0.002
Level-3	The centralized drinking water sources; industrial uses and agricultural uses			≤0.5	≤20	≤0.02
Level-4	Agricultural uses; certain industrial uses; potable water after treatment			≤1.5	≤30	≤0.1
Level-5	Not suitable as drinking water sources, selected for other uses with different purposes			>1.5	>30	>0.1

Figure 12: The test results of pH (a), EC (b), and ammonia concentration (c) in rainwater, river water, and groundwater.

reflecting the influence of anthropogenic activities. Nitrate, a ubiquitous contaminant of natural water resources that is mainly caused by agricultural activities such as the application of fertilizer and manure [16,34,59], varies within a large range from 0.01 to 102.00 mg/L (nitrate-N) in the local phreatic groundwater; 23.7% (14 of 59) of the samples are attributed to the lowest level of the standard for groundwater quality of P. R. China [40] (Level-5), 10 of which were sampled from the farmland (Figure 10b). The test results of Pb, Hg, Zn, Cu, Cd, and Ni indicate that the local phreatic groundwater is slightly polluted by heavy metals; 8.5% (5/59) of the sampling sites show detected concentrations attributing to Level-5 [40] (3 for Pb and 2 for Ni; Figure 10c and d), while the test results of other samples are superior to Level-3. It should be noted that the high levels of ammonia, nitrate, and heavy metals are mainly concentrated in the same regions such as the well nos. 4–7, 42–46, and 54–59 (Figure 10), suggesting a point-source pollution trend. Field investigation indicates that the regions of the groundwater sampling well nos. 4–7 and 54–59 have a landfill and an industrial park, which would be the potential pollution source of the regional phreatic groundwater.

The sampling and analysis results indicate that the chemical composition of the local phreatic groundwater is affected by both natural and anthropogenic processes; however, it is still difficult to precisely evaluate the process contributions for each sample because the major compounds in groundwater could come from either source [6,58]. Studies used the indicative features of some specific ions such as the concentration level and distribution characters to reveal the origin of groundwater components; in particular, fluoride and nitrate compositions can

be important indicators of natural versus anthropogenic sources, respectively [6,16,58]. Batch experiments on the dissolution of granite and biotite conducted by Chae et al. [58,60] indicated that F-bearing biotite may be the primary source of high fluoride concentrations in groundwater; thus, fluoride in the local groundwater may probably have originated from the natural water–rock interactions. However, the concentrations of fluoride display an inverse relationship on the Piper plots compared with nitrate, which largely originates from the diffuse (non-point) sources relating to agricultural and domestic practices, as well as the point sources such as sewage effluent [58] as discussed before. Figure 11 shows that the hydrochemical facies of the samples with high concentrations of fluoride is mainly Ca–Mg–HCO₃, while nitrate is enriched in the Ca–SO₄–Cl type of groundwater, suggesting different origins of fluoride and nitrate in the local groundwater. In fact, the human activities as mentioned above influence the natural groundwater quality, generally leading to increased chloride, sulfate, and nitrate [58,61,62]; thus, the Ca–SO₄–Cl type of groundwater represents the anthropogenic contamination in the local phreatic groundwater, and this result is in agreement with the research conducted by Kim et al. [58] in a bedrock aquifer in South Korea.

4.5 Conceptual model of the chemical evolution of the local phreatic groundwater

Precipitation and river leakage are the primary recharge sources of the phreatic groundwater; thus, the chemical characters of the groundwater are undoubtedly related

to the rainwater and river water [6,56,58]. Figure 12 shows the test results of pH, EC, and ammonia concentration in rainwater, river water, and groundwater, suggesting that all of the average values of these parameters in the groundwater are within the average values in the rainwater and river water. For instance, the average values of pH in the rainwater and river water are 5.88 and 7.30, and it is 6.55 in the groundwater (Figure 12a), while the average values of EC and ammonia are 14.1, 492.7, and 357.7 $\mu\text{S}/\text{cm}$ (Figure 12b) and 0.68, 2.45, and 1.03 mg/L in the rainwater, river water, and groundwater (Figure 12c), respectively. Though buffered by the vadose zone, weakly acid precipitation recharging the phreatic groundwater would probably affect its acid-alkali condition, which may further accelerate the dissolution of calcite and dolomite, which would be a possible reason for the relatively high concentrations of Ca^{2+} in the local groundwater. EC is a rough parameter that reveals the dissolved solid concentration of the water samples; increased average values of the river water samples compared with the rainwater and groundwater suggest chemical substance imports into the L.R.; approximate tendency of the test results of ammonia indicates that the water quality of the L.R. is affected by human activities which may potentially be

one of the pollution sources of the local phreatic groundwater.

Despite the lack of isotope sampling and test results which can reveal the groundwater supply source precisely, a conceptual model (Figure 13) that generalizes the hydrochemical evolution and potential pollution sources of local phreatic groundwater is built according to the study results mentioned above. The precipitation is the major freshwater supply source of the L.R. and local groundwater, with construction land and farmland occupying c. 58% of the whole area of the L.R. basin; human activities play a vital role in local water environment. The L.R. flows from southwest to northeast with increasing concentration of ammonia, suggesting the river water quality is influenced by anthropogenic pollution such as the sewage effluence, which may potentially affect the groundwater quality through surface water-groundwater interchange; meanwhile, the infiltration and leakage of the point source such as the industrial park and the landfill may increase the pollution risk of the local groundwater, as proved by the distribution of the high concentration of ammonia and heavy metals at sampling sites; agricultural activities including fertilizer and manure application result in non-point-source pollution of groundwater as illustrated

Figure 13: Conceptual model of the chemical evolution of the local phreatic groundwater affected by natural and anthropogenic factors.

Figure 11: Piper plots of the phreatic groundwater of the study area with relative concentrations of (a) fluoride and (b) nitrate (blue and red dots, respectively).

in Figure 10b. The high nitrate concentration at sampling sites is mainly distributed in the farmland (the middle regions of the L.R. basin); moreover, pumping groundwater for irrigation enhances the leaching/infiltration of soil–water and accelerates the groundwater flow which further promotes the water–rock interactions, possibly leading to the dissolution of the soluble rocks and an increase in Ca^{2+} and HCO_3^- in groundwater. In general, both natural and anthropogenic factors dominate the phreatic groundwater geochemical evolution of the L.R. basin; the lithology, hydrogeological conditions, and water–rock interactions determine the hydrochemical facies, while pollution due to the effluent discharged into the L.R. from industrial manufacturing activities as well as the consumption of fertilizer leads to the deterioration in the local phreatic groundwater quality indirectly. The results presented herein will facilitate the development of plans to sustainably use and protect local groundwater. Moreover, further studies to identify the factors dominating the groundwater quality are warranted.

5 Conclusions

1. With slightly acidic and aerobic conditions, Ca^{2+} , HCO_3^- , and SO_4^{2-} dominate the chemical components of the phreatic groundwater of the L.R. basin, and Ca-Mg-HCO_3 , Ca-Na-HCO_3 , Na-Ca-HCO_3 , Na-HCO_3 , and $\text{Na-SO}_4\text{-Cl}$ are the major hydrochemical facies.

2. Water–rock interactions such as the dissolution of calcite and dolomite are the primary source of the major ions in the local groundwater, and cation-exchange reaction has its effects on the levels of Ca^{2+} , Mg^{2+} , and Na^+ .
3. Anthropogenic factors play a vital role in the chemical evolution of the local river water and groundwater; the pollution discharge such as the sewage effluence results in the marked increase in the concentration of ammonia in the L.R. along the flow direction.
4. Different land-use types represented by industrial manufacturing and agricultural activities in the L.R. basin are related to the deterioration in the local groundwater quality, indicating high concentrations of nitrate and heavy metals in the groundwater of the farmland and the construction land.

To ensure local water environment safety, the supervision of the point sources such as the industrial park and the landfill site in the L.R. basin should be emphasized and the application of fertilizer and manure should be restricted further.

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