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Hydrochemical and Isotope (^{18}O , ^2H and ^3H) Characteristics of Karst Water in Central Shandong Province: A Case Study of the Pingyi-Feixian Region

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Abstract: Karst water serves as an important water supply source in northern China. Hydrochemical and isotope (^{18}O , ^2H , and ^3H) characteristics are invaluable tools to identify water–rock interaction activities in karst water systems. In this study, the investigation of hydrogeological conditions, hydrogeochemistry, and hydrogen and oxygen isotopes of karst water revealed: (1) $\text{HCO}_3\text{-Ca}$ -type water is widely distributed throughout the study area, while $\text{HCO}_3\text{-Ca-Mg}$ -type water appears in the direct recharge areas and the discharge areas; karst water of the $\text{HCO}_3\text{-Cl}^-$, $\text{Cl}^- \cdot \text{HCO}_3^-$, and Cl^- types is scattered in low-land areas; (2) karst water has high $\delta^{18}\text{O}$, which may be due to the dissolution and exchange of ^{18}O from the surrounding carbonate rocks in the western discharge zone; and (3) the ^3H concentration of karst water is strongly correlated with the content of major ions (Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , and Cl^-) and it increases along the flow path. It was also revealed that the karst water in the discharge areas is mixed with lateral recharge (infiltration recharge from surface water).

Keywords: karst water; water–rock interaction; hydrochemical characteristics; isotope (^{18}O , ^2H , and ^3H)

1. Introduction

Each karst water system has its own storage, transport, and regulatory functions and constantly exchanges water with other system components, resulting in changes in water quantity and quality as the entire system interacts with the external environment [1–14].

The hydrochemical characteristics of karst water, as well as the isotope (^{18}O , ^2H , and ^3H), are direct indicators of spatial variations in water quantity and quality [15–23]. The hydrochemistry of karst water is generally focused on the distribution of major ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , and Cl^-). ^2H and ^{18}O are stable isotopes that are widely used to retrieve information about the sources, areas, and times of karst water recharge. This information is acquired by comparing the isotope composition of karst water with that in global or regional water bodies, indicating the recharge source of karst water. ^3H is a natural radioactive isotope of hydrogen with a half-life of 12.32 years. Due to atmospheric nuclear tests in the 1950s and in the early 1960s, the ^3H concentration in precipitation increased sharply; it peaked at 1868 TU in 1963 [24] and declined every year until reaching 32 TU in 2001 (from the precipitation monitoring station of IAEA in Shijiazhuang), identifying ^3H as a good indicator of whether the recharge sources of karst water formed before or after these nuclear tests (1952). In recent years, a large number of karst water studies have explored the structures, hydrodynamic processes, and hydrochemical evolution patterns of

karst water systems based on analyses and measurements of major ions and isotopes (^{18}O , ^2H , and ^3H), especially in the karst water areas of northern China [25–39].

In this case study, a hydrogeological survey, with a scale of 1/50,000, was carried out in the Pingyi–Feixian region at central Shandong Province, China. The aim of this study was to reveal the spatial distribution characteristics of major ions and isotopes (^{18}O , ^2H , and ^3H) to provide insight into the hydrochemical evolution patterns of the karst water system.

2. Hydrogeological Setting of Karst Water in the Study Region

2.1. Geological Setting

The Pingyi–Feixian karst region in the central zone of Shandong Province, China, is situated at $117^{\circ}30'–118^{\circ}00'$ E and $35^{\circ}10'–35^{\circ}30'00''$ N, and it covers 596 km^2 . According to monitoring data from the Feixian and the Pingyi meteorological stations, in Shandong Province from 1971 to 2013 the annual mean precipitation in the area is 798 mm and the annual mean evapotranspiration is 1536 mm. The precipitation from June to August accounts for approximately 65% of the annual precipitation. As shown in Figure 1, the region is characterized by hilly landforms, with a surface elevation of 100–500 m, and the strata generally dip toward the north and east, which is consistent with the topography.

Figure 1. Geological structure map of the study region.

The region has the following karstic formations composed of thick carbonate rocks: (1) the Mantou Formation (ϵ_2m) of the Changqing Group; (2) the Gushan Formation (ϵ_{3-4g}), the Zhangxia Formation (ϵ_3z), the Chaomidian Formation (ϵ_4O_1c), and the a, b, and c sections of the Sanshanzi Formation (O_1s^a , O_1s^b , and O_1s^c) of the Jiulong Group; and (3) the Dong Huangshan Formation (O_2d), Bei'an zhuang Formation (O_2b), Tuyu Formation (O_2t), Wuyangshan Formation (O_2w), Gezhuang Formation (O_2g), and Badou Formation (O_{2-3b}) of the Majiagou Group. Moreover, the region is covered by Quaternary deposits on

both banks of the Junhe River, Zhutian River, and Wenliang River and in near low-lying valleys. Strata of Neogene, Cretaceous, and Carboniferous are distributed sporadically in the relatively flat zone in the northern part of the study area. Intrusive rocks and metamorphic rocks are mainly distributed in the low mountainous zones in the middle and southern regions of the study area. There are a series of fault structures in the southeast direction and four deep faults in the north and south directions.

2.2. Hydrogeological Characteristics of Karst Aquifers

Combining the previous research and the findings of this study, the karst region was divided into six zones according to hydrogeological conditions (Figure 2): two direct recharge zones, one indirect recharge zone, and three discharge zones [40].

Figure 2. Zoning of the study region based on the hydrochemical characteristics of karst water.

The direct recharge zones consist of zones W and E, which are situated in the Changli–Dongyang area of Pingyi County and the Zhutian–Yuanwai area of Feixian County, respectively. The karst landscape is characterized by clustered hill valleys with hilly and low-mountain terrain in which seasonal rivers are distributed in a plumose pattern. The strata lithology is mainly limestone and dolomite intercalated with shale ranging from the Mantou Formation of the Changqing Group to the Sanshan Formation of the Jiulong Group. The strata are mostly bare, with a precipitation infiltration coefficient of 0.17–0.21, referring to the ratio of the amount of water infiltrated by precipitation to the amount of precipitation in the same period [40]. Surface karst landforms such as karst grooves and crevices are widespread, allowing a large amount of precipitation to directly infiltrate the underground karst water system as recharge.

The indirect recharge zone, which is situated in the Changli–Zhangli–Tongshi area in the middle of the study region, has a hilly and low-mountain terrain. The strata lithology

is mainly metamorphic rocks such as gneiss, granite, and diorite porphyrite formed in the Upper Archean, as well as intrusive rocks formed at various stages. Some areas in the zone are partly covered with Cambrian carbonate rocks intercalated with mud shale. The precipitation infiltration coefficient in this region is 0.05–0.08 [40]. A small amount of precipitation infiltrates as groundwater recharge, forming shallow weathering fissure water, while most precipitation forms surface runoff that enters carbonatite-dominated areas, where the surface water infiltrates the karst aquifer as recharge.

The discharge zones consist of zones W, E, and S, which are situated in the Dongyang–Wenshui area of Pingyi County, the Difang–Chengbei area of Feixian County, and the urban area of Feixian County, respectively. The landforms are characterized by karst basins with loose surface Quaternary deposits and low-lying valleys. The karst strata are mainly limestone, dolomite, and argillaceous limestone (occasionally containing gypsum) of the Majiagou Group with well-developed karst crevices, pores, and caves in which the water yield of a single well exceeds 1000 m³/d.

2.3. Exploitation of Karst Water

Karst water is mainly used for agricultural irrigation in the Dongyang–Wenshui area of Pingyi County inside zone W and for urban residential consumption in the Difang–Chengbei area of Feixian County inside zone E. It is extracted from motor-pumped wells and the water yield of a single well is generally less than 300 m³/d, although it can reach as high as 2.4×10^3 m³/d for domestic water plants in Feixian County.

The total exploitation volume of karst water in 2013 and in 2015 was 82.2 million m³ and 108.9 million m³, respectively, increasing by 18.9% to 144.3 million m³ in 2017. In this study, the whole area was divided into nine units (C1–C9) according to hydrological conditions and the extraction modulus (defined as the volume of karst water extracted per km² and year) was calculated for each unit. As shown in Figure 3, the extraction moduli of karst water in the units ranged from 2.48×10^4 m³/(a·km²) to 28.07×10^4 m³/(a·km²) in 2017. Notably, the extraction modulus exceeded 20×10^4 m³/(a·km²) in both the Wenshui unit (C1) of Pingyi County and the Feixian County unit (C6), where artificial extraction is relatively concentrated, followed by 15.21×10^4 m³/(a·km²) in C1 and less than 10×10^4 m³/(a·km²) in other units.

Figure 3. Zoning of the study region to calculate the extraction modulus of karst water.

3. Materials and Methods

In this study, 78 karst water samples were collected in the direct recharge zones: 22 karst water samples in the indirect recharge zone and 32 karst water samples in the discharge zones (Figure 4). The sampling period for 28 typical samples of major ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , and Cl^-) and isotopes (^{18}O , ^2H and ^3H) was October–November 2013. The sampling depth was 0–370 m in boreholes (Table 1). The sampling sites were selected so the upstream–downstream relationship of karst water in the region would be revealed by subsequent analyses.

During sampling and testing of the karst water, three samples were collected at each sampling site, placed in airtight 1.0 L polyethylene plastic bottles without head space, and stored. ^{18}O , ^2H and ^3H isotope measurements were conducted at the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences.

The detection of major ions in water adopted the standardized method of China's geology and mineral industry. Flame emission spectrometry was used to determine K^+ and Na^+ , ethylenediamine tetraacetic acid disodium titration was used for Ca^{2+} and Mg^{2+} , argentometric titration for Cl^- , ethylenediamine tetraacetic acid disodium–barium titration for SO_4^{2-} , and acidimetry acid titration for HCO_3^- . Specifically, water $\delta^{18}\text{O}$ was measured using the $\text{CO}_2\text{--H}_2\text{O}$ equilibration method, while water $\delta^2\text{H}$ was determined using the

chromium reduction method. The analyses were conducted using a MAT-253 Gas Isotope Ratio Mass Spectrometer with a precision of $\sigma \leq 0.1\%$ and $\sigma \leq 2\%$, respectively. The water concentration of ^3H was determined by the electrolytic concentration method using an ultra-low background 1220 Quantulus liquid scintillation spectrometer with a precision of $\sigma \leq 0.6$ TU.

Figure 4. Karst water sampling sites in the study region.

Table 1. Typical hydrochemical and isotopic samples of precipitation and karst water.

Sample No.	Sampling Date	Sampling Location	Sampling Depth (m)	Notes
Fxj	November 2013	Feixian County		Precipitation
SW134	November 2013	Pingyi County	85–200	Indirect recharge zone
SW136	November 2013	Pingyi County	9–88	
SW137	November 2013	Pingyi County	8–27	
DW018	November 2013	Pingyi County	60–187	Direct recharge zone(W)
DW110	November 2013	Pingyi County	18–26	
DW111	November 2013	Pingyi County	0–141	
DW130	November 2013	Pingyi County	14–170	

Table 1. Cont.

Sample No.	Sampling Date	Sampling Location	Sampling Depth (m)	Notes
FK03-1	October 2013	Feixian County	4–32	Direct recharge zone(E)
FW281	November 2013	Feixian County	30–73	
FW237A	October 2013	Pingyi County	80–100	
FW332	October 2013	Feixian County	18–80	
FW071	October 2013	Feixian County	50–120	
FW073	October 2013	Feixian County	0–88	
FW237	October 2013	Pingyi County	80–100	
FW087	November 2013	Feixian County	40–170	
FK03	October 2013	Feixian County	29–202	
FK01	October 2013	Feixian County	80–325	
FW232	November 2013	Feixian County	200–370	
DW093	November 2013	Pingyi County	28–40	Discharge zone(W)
DW094	October 2013	Pingyi County	16–20	
DK03A	October 2013	Pingyi County	0–301	
DW007	October 2013	Pingyi County	40–150	
DW100	November 2013	Pingyi County	180	
DW102	November 2013	Pingyi County	150	
DK03	October 2013	Pingyi County	0–301	
SW018	October 2013	Feixian County	15–88	Discharge zone(E)
FW110	October 2013	Feixian County	20–200	
SW216	October 2013	Feixian County	15–200	

4. Results and Discussion

4.1. Hydrochemical Characteristics of Karst Water

Water samples were subjected to hydrochemical classification based on the values of the major ions (Schukalev classification), as shown in Table 2 and in Figures 5 and 6a,b. Karst water types in the study area included the $\text{HCO}_3\text{-Ca}$ type, $\text{HCO}_3\text{-SO}_4\text{-Ca}$ type, and $\text{HCO}_3\text{-Ca-Mg}$ type. The water type was found to mainly be $\text{HCO}_3\text{-Ca}$ -type and $\text{HCO}_3\text{-SO}_4\text{-Ca}$ type in the indirect recharge zone, while the main karst water types in the direct recharge and discharge zones were found to be $\text{HCO}_3\text{-Ca-Mg}$ and $\text{HCO}_3\text{-Ca}$. Direct recharge zone E and discharge zone E, which are both in the eastern portion of the study region, were found to have a significantly higher proportion of $\text{HCO}_3\text{-Ca-Mg}$ -type karst water than that in western direct recharge zone W and discharge zone W. Among the anions accounting for greater than 25% of the total, HCO_3^- was found to be widespread in the whole study area, with a combination of HCO_3^- and SO_4^{2-} mainly distributed in the central portion, which mainly features exposed metamorphic rocks of gneiss, granite, diorite porphyrite, and intrusive rocks, while Cl^- was found to be distributed sporadically in low-lying area. Cations were found to have a more obvious distribution pattern in the study region, with karst water abundant in both Ca^{2+} and Mg^{2+} primarily distributed in the main flow zones.

The distribution frequencies of TDS in karst water are shown in Figure 6c. The karst water samples of the indirect recharge zone presented TDS levels in the range of 248–1949 mg/L, of which samples with TDS levels of 400–500 and 500–600 mg/L accounted for 32% and 18%, respectively. The direct recharge zones had karst water TDS levels in the range of 323–899 mg/L: 400–500, 500–600, and 600–700 mg/L constituted the major intervals, especially for direct recharge zone E, where such water samples accounted for 35%, 31%, and 28% of the total samples, respectively. The karst water samples of the discharge zones had TDS levels in the range of 278–1059 mg/L, of which samples with TDS levels of 500–600 mg/L and 600–700 mg/L accounted for 49% and 32%, respectively. In particular, samples with TDS levels of 500–600 and 600–700 mg/L accounted for the highest proportions, with 55% and 48% in discharge zones W and E, respectively.

Table 2. Chemical composition of the water samples.

Sample No.	pH	$\delta^2\text{H}$ (‰)	$\delta^{18}\text{O}$ (‰)	^3H (TU)	TDS (mg/L)	K^+ (mg/L)	K^+ (mmol/L)	Na^+ (mg/L)	Na^+ (mmol/L)	Ca^{2+} (mg/L)	Ca^{2+} (mmol/L)	Mg^{2+} (mg/L)	Mg^{2+} (mmol/L)	HCO_3^- (mg/L)	HCO_3^- (mmol/L)	SO_4^{2-} (mg/L)	SO_4^{2-} (mmol/L)	Cl (mg/L)	Cl (mmol/L)	Notes
Fxj	/	−60	−9.2	12.6	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	Precipitation
SW134	7.6	−64	−8.3	7.2	678.2	0.89	0.023	16.7	0.72	120.4	3.01	26.5	1.10	288.7	4.73	73.1	0.76	36.5	1.03	Indirect recharge zone
SW136	7.2	−62	−8.0	8.9	1949.2	1.56	0.040	66.7	2.90	415.5	10.39	71.1	2.96	254.2	4.17	188.6	1.96	410.3	11.56	
SW137	7.4	−56	−7.3	8.0	929.6	1.11	0.028	32.0	1.39	175.8	4.39	32.3	1.35	389.1	6.38	91.9	0.96	86.6	2.44	
DW018	7.4	−60	−8.3	10.9	859.9	1.11	0.028	20.0	0.87	157.8	3.95	32.7	1.36	375.6	6.16	73.1	0.76	54.7	1.54	Direct recharge zone(W)
DW110	7.3	−62	−8.1	9.2	695.4	1.11	0.028	10.0	0.43	110.9	2.77	34.6	1.44	304.7	4.99	26.9	0.28	56.0	1.58	
DW111	7.8	−59	−8.0	10.7	519.7	0.44	0.011	7.5	0.33	107.9	2.70	13.6	0.57	263.9	4.33	36.7	0.38	38.3	1.08	
DW130	7.5	−62	−8.8	5.5	898.7	0.67	0.017	26.2	1.14	186.8	4.67	23.0	0.96	355.2	5.82	82.5	0.86	69.9	1.97	
FK03–1	7.8	−58	−8.1	8.3	793.2	0.33	0.008	14.2	0.62	129.2	3.23	45.7	1.90	375.4	6.15	61.2	0.64	41.3	1.16	Direct recharge zone(E)
FW281	7.4	−61	−8.7	7.1	554.2	0.44	0.011	2.5	0.11	121.1	3.03	11.1	0.46	323.7	5.31	34.3	0.36	17.7	0.50	
FW237A	7.6	−60	−8.5	7.8	964.2	0.33	0.008	20.0	0.87	199.4	4.99	22.8	0.95	424.4	6.96	97.9	1.02	59.0	1.66	
FW332	7.9	−59	−8.4	7.1	1167.3	1.22	0.031	36.0	1.57	215.7	5.39	39.5	1.65	375.4	6.15	257.1	2.68	64.9	1.83	
FW071	7.7	−60	−8.5	6.0	596.8	0.33	0.008	13.3	0.58	104.0	2.60	28.0	1.16	263.6	4.32	61.3	0.64	36.5	1.03	
FW073	7.4	−62	−8.6	8.9	579.8	0.33	0.008	3.3	0.14	108.9	2.72	22.8	0.95	350.9	5.75	31.8	0.33	13.3	0.37	
FW237	7.4	−61	−8.5	8.1	662.6	0.22	0.006	4.2	0.18	132.3	3.31	23.5	0.98	296.5	4.86	63.7	0.66	13.3	0.37	
FW087	8.0	−61	−8.3	8.5	586.8	0.44	0.011	7.5	0.33	108.9	2.72	26.5	1.11	266.6	4.37	80.8	0.84	25.1	0.71	
FK03	7.5	−59	−8.2	10.1	718.9	0.44	0.011	11.7	0.51	121.1	3.03	39.5	1.65	353.6	5.80	49.0	0.51	41.3	1.16	
FK01	7.7	−61	−8.6	7.1	579.5	1.33	0.034	8.8	0.38	86.5	2.16	35.8	1.49	353.6	5.80	31.8	0.33	16.2	0.46	
FW232	7.9	−62	−8.6	7.1	533.9	0.44	0.011	5.0	0.22	84.4	2.11	32.7	1.36	238.5	3.91	68.4	0.71	13.7	0.39	
DW093	7.2	−70	−8.9	7.4	868.1	0.22	0.006	13.3	0.58	183.0	4.57	16.5	0.69	414.2	6.79	66.0	0.69	45.6	1.28	Discharge zone(W)
DW094	7.5	−59	−8.2	9.2	681.7	1.44	0.037	15.0	0.65	122.1	3.05	26.5	1.11	302.0	4.95	53.9	0.56	50.1	1.41	
DK03A	7.4	−59	−8.3	8.4	725.6	0.44	0.011	10.8	0.47	143.5	3.59	22.2	0.93	402.6	6.60	46.5	0.48	35.4	1.00	
DW007	7.6	−61	−8.5	12.2	714.3	0.44	0.011	7.9	0.34	147.5	3.69	21.0	0.87	315.6	5.17	61.2	0.64	32.4	0.91	
DW100	7.7	−56	−7.6	9.6	656.0	0.44	0.011	11.7	0.51	130.2	3.26	18.5	0.77	302.0	4.95	46.5	0.48	38.3	1.08	
DW102	7.5	−59	−8.3	6.7	880.5	0.56	0.014	15.0	0.65	176.9	4.42	32.3	1.35	379.7	6.22	47.1	0.49	92.7	2.61	
DK03	7.9	−60	−8.4	8.1	500.1	0.33	0.008	5.8	0.25	93.6	2.34	20.4	0.85	236.7	3.88	39.2	0.41	26.5	0.75	
SW018	7.6	−60	−8.3	10.9	530.5	0.56	0.014	9.2	0.40	99.7	2.49	16.7	0.69	269.3	4.41	39.2	0.41	25.1	0.71	Discharge zone(E)
FW110	7.4	−58	−8.0	8.1	606.4	1.7	0.044	15.0	0.65	108.5	2.71	21.9	0.91	315.5	5.17	60.8	0.63	31.9	0.90	
SW216	7.6	−58	−8.0	9.0	535.7	1.22	0.031	9.2	0.40	100.7	2.52	21.0	0.87	269.3	4.41	46.5	0.48	29.5	0.83

Figure 5. Piper trilinear diagram for the classification of karst water in each zone.

4.2. ^2H and ^{18}O Isotope Characteristics of Karst Water

As shown in Table 2, the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of karst groundwater ranged, respectively, from -70‰ to -56‰ , with an average of -60‰ , and from -8.8‰ to -7.3‰ , with an average of -8.3‰ . As shown in Figure 7, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of karst water in the entire region were roughly distributed along the meteoric water lines, reflecting that the regional groundwater originated from precipitation. The $\delta^{18}\text{O}$ - $\delta^2\text{H}$ line of the study region was below the global meteoric water line [41], the China meteoric water line [27], and the meteoric water line of Shijiazhuang (Hebei Province), which is typical of northern China [42] and indicative of a continental effect. Specifically, the karst water in the study region underwent strong evaporation, thereby deviating from the global meteoric water line.

Linear regression of karst water $\delta^2\text{H}$ against karst water $\delta^{18}\text{O}$ for each zone revealed that the line fitting the indirect recharge zone was most similarly shaped to the meteoric water lines, followed by the lines fitting the discharge zones; while, the lines fitting the direct recharge zones had significantly smaller slopes than the meteoric water lines, reflecting that the water–rock interaction is weakest in the indirect recharge area and that the karst water in the direct recharge area features significant solution filtration in the runoff process, thereby increasing the degree of ^{18}O isotope fractionation in the karst water.

The measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and the fitting lines for direct recharge zone E coincided well with those of discharge zone E, suggesting good runoff conditions in the two zones and, therefore, rapid karst water recharge. The $\delta^{18}\text{O}$ values of discharge zone W were greater than those of direct recharge zone W, suggesting the karst water underwent strong evaporation after the recharge of precipitation in this zone in which the main outcrop is composed of limestone and dolomite intercalated with shale from the Mantou Formation of the Changqing Group to the Chaomidian Formation of the Jiulong Group. Moreover, the vadose zone is widely distributed in direct recharge zone W, where the vadose water undergoes evaporation and thus has a higher $\delta^{18}\text{O}$ than precipitation. Such vadose water provides leakage recharge to deep karst water, thereby increasing the karst water $\delta^{18}\text{O}$. The slope of the fitting line of direct recharge zone E was close to the slopes of the meteoric water lines but significantly greater than the slope of direct recharge zone W, indicating a weaker evaporation effect on karst water in direct recharge zone E compared to direct

recharge zone W. The $\delta^{18}\text{O}$ – $\delta^2\text{H}$ fit of discharge zone E coincided with that of discharge zone W, suggesting the karst water of discharge zone E features a similar ^{18}O and ^2H isotope composition to that of discharge zone W due to joint recharge from precipitation infiltration and river water leakage.

Figure 6. Distribution of hydrochemical types of karst water. (a) Zoning of the study region based on the hydrochemical types of karst water; (b) The proportion of hydrochemical types in the total number of samples in each zone; (c) The proportion of TDS levels in the total number of samples in each zone.

Figure 7. Scatter plots of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ of karst water.

4.3. ^3H Isotope Characteristics of Karst Water

As shown in Table 2, the ^3H concentration in precipitation is 12.6 TU, which is significantly higher than that in karst water (by 5.5–12.2 TU), indicating the ^3H concentration decreased naturally in the process of precipitation supplying karst water. Moreover, the ^3H concentration of the karst water samples was observed to have the following major relationships with the five zones (Figure 8):

- (1) The ^3H concentration generally increased with an increase in runoff distance. The lowest concentration was observed at the boundaries of karst watersheds (i.e., sampling sites DW130 and FW071). Sampling sites with ^3H concentrations <7.5 TU were found to be mainly located at the front edge of the direct recharge zones (i.e., sampling sites FW281, FW232, FW332, and FK01). Sampling sites with ^3H concentrations of 7.5–8.5 TU were located primarily inside the direct recharge zones (i.e., sampling sites FW237A, FW237, FK03-1, and FW087), while sampling sites with ^3H concentrations of 9.0–12.5 TU were principally inside the discharge zones and at some near-boundary areas of the direct recharge zones relative to the discharge zones.
- (2) Discharge zones W and E both had significantly lower ^3H concentrations distributed in a belt-like pattern. These low-value areas coincided with areas featuring the large-scale artificial extraction of karst water, indicating that karst water extraction induced old karst water that flowed from the aquifer to the extraction areas.
- (3) Changes in ^3H concentrations were larger closer to large-scale extraction areas.

Figure 8. Distribution characteristics of the tritium (^3H) values of karst water.

4.4. Hydrochemical Evolution of Karst Water

The dissolution of rocks and the precipitation of ions in the karst water during karst water flow determine the concentrations of major ions (Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , and Cl^-). However, the ^3H in karst water is supplied by precipitation and surface water, and its concentration increases with an increase in cumulative recharge. Together, the dynamics of ^3H and major ions represent the hydrodynamic characteristics of karst water.

4.4.1. Dissolution and Precipitation of Carbonate Rocks

The concentrations of Ca^{2+} , Mg^{2+} , and HCO_3^- are mainly subject to carbonate rock erosion by CO_2 -rich karst water and the precipitation process. The relationship between the Ca^{2+} molar concentration and ^3H concentration is shown in Figure 9a. Because of the large amount of surface water infiltration recharge to karst aquifers in direct recharge zone E and discharge zone E of the eastern study region, Ca^{2+} ions are mostly dissolved during karst water flow. Moreover, sampling sites FW237A and FW332 exhibited significantly higher concentrations of Ca^{2+} and SO_4^{2-} relative to the surrounding sampling sites, which suggests that, in addition to the dissolution of carbonate rocks, the two sampling sites were simultaneously influenced by the dissolution of CaSO_4 intercalated in the carbonate.

However, the Ca^{2+} molar concentration was negatively correlated with the ^3H concentration in direct recharge zone W and discharge zone W, indicating the karst aquifers in these zones were mainly recharged by deep lateral flow from outside the study region, while Ca^{2+} in the karst water underwent precipitation during the recharge process. The relationship of the Mg^{2+} molar concentration versus ^3H concentration, which is shown in Figure 9b, suggests three different patterns: (1) the intensive dissolution and leaching of Mg^{2+} from carbonate rocks in direct recharge zone E; (2) the significant dilution of Mg^{2+} in discharge zone E by a large amount of karst water discharged from upstream; and (3) a relatively stable Mg^{2+} molar concentration in direct recharge zone W and discharge zone W, where the dilution effect of karst water recharge from surface water infiltration is offset by the dissolution and leaching of Mg^{2+} from the surrounding rocks.

Changes in the ratio of Ca^{2+} and Mg^{2+} molar concentrations (Figure 9c) further confirm that direct recharge zones E and W gradually experience a transition from carbonate mineral dissolution to calcium ions precipitation under the flow of karst water. Specifically, as the free CO_2 in karst water is gradually exhausted and the erosivity of karst water is weakened during the interactions of karst water with rocks, calcium ions precipitation gradually increases and the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio decreases. The positive correlation between $\text{Ca}^{2+}/\text{Mg}^{2+}$ and the ^3H concentration in discharge zones E and W suggests a large amount of CO_2 -rich precipitation infiltrates as recharge to karst aquifers, thereby increasing the dissolution of Ca^{2+} .

There is a positive correlation between the HCO_3^- molar concentration and ^3H concentration (Figure 9d) in direct recharge zone E, where karst aquifers continue to receive a large amount of surface infiltration recharge as surface runoff flows carrying CO_2 and ^3H into karst water. In contrast, there is a negative correlation between the HCO_3^- concentration and ^3H concentration in direct recharge zone W and in discharge zones W and E. This result indicates that strong water–rock interactions occur in the lateral runoff of the deep karst aquifers such that the increased HCO_3^- concentration due to surface infiltration recharge fails to compensate for the consumed HCO_3^- concentration during lateral flow recharge, thereby decreasing the HCO_3^- concentration in karst water.

4.4.2. Dissolution of Sulfate Rocks

As shown in Figure 10a, there is a negative correlation between the SO_4^{2-} molar concentration and ^3H concentration in direct recharge zones E and W, as well as in discharge zone E, indicating the SO_4^{2-} that dissolved and leached from rocks during the water–rock interaction was diluted by surface infiltration recharge. In contrast, the SO_4^{2-} molar concentration was found to be positively correlated with ^3H in discharge zone W, suggesting the presence of higher strength water–rock interactions leading to the dissolution and leaching of SO_4^{2-} when compared with other zones. In addition, the scatter plot of SO_4^{2-} versus Ca^{2+} (Figure 10b) shows the data points reflecting the molar concentrations of SO_4^{2-} and Ca^{2+} in karst water were significantly below the gypsum dissolution line of slope 1:1. However, the scatterings in the eastern area of the direct recharge area are close to a 1:1 straight line, indicating the concentration of Ca^{2+} released from the gypsum is far less than that produced by the limestone in the study area and that gypsum dissolution is stronger in recharge zone E than in other areas.

(c)

Figure 9. Cont.

Figure 9. Correlation between the concentration of ^3H and major carbonate rock-related ions in karst water. (a) Correlation between the concentration of ^3H and Ca^{2+} ; (b) Correlation between the concentration of ^3H and Mg^{2+} ; (c) Correlation between the concentration of ^3H and the ratio of Ca^{2+} and Mg^{2+} ; (d) Correlation between the concentration of ^3H and HCO_3^- .

4.4.3. Dissolution of Chlorides

Except for the abnormally high Cl^- concentration at SW136, the Cl^- concentration in the study area was found to range from 13.27 to 92.67 mg/L due to the dissolution of soluble halite rocks intercalated between mudstone and shale interbeds in the carbonate rocks. The karst water level is shallow and the evaporation is strong in the low-lying shallow discharge zones, leading to high Cl^- concentrations. Additionally, there is a decrease in Cl^- concentration with an increasing ^3H concentration (Figure 11) in each zone, indicating the continuous dilution of Cl^- as a readily soluble and migratable component in the flow process of karst water.

Figure 10. Cont.

Figure 10. Correlation between the concentration of ^3H and major sulfate rock-related ions in karst water. (a) Correlation between the concentration of ^3H and SO_4^{2-} ; (b) Correlation between the concentration of Ca^{2+} and SO_4^{2-} .

Figure 11. Correlation between the concentration of Cl^- and ^3H concentration in karst water.

5. Conclusions

Based on the hydrochemical and isotope (^{18}O , ^2H and ^3H) investigation of karst water, the following conclusions can be provided:

- (1) Shallow karst water of the $\text{HCO}_3\text{-Ca}$ type with a short flow path is ubiquitous in the study region, while karst water of the $\text{HCO}_3\text{-Ca}\cdot\text{Mg}$ type with a long flow path is present in both the direct recharge and discharge zones. The interactions of karst water with carbonate, sulfate, and halite result in a variety of hydrochemical processes such as dissolution, precipitation, mixing, and dilution. Overall, karst water has a slightly lower degree of mineralization in the direct recharge zones than in the discharge zones. In contrast, the indirect recharge zone suffers from a relatively closed condition with TDS up to 1949 mg/L, indicative of long-term water–rock interactions.
- (2) The $\delta^{18}\text{O}$ - $\delta^2\text{H}$ fitting line of karst water in the indirect recharge zone has the closest slope to the meteoric water lines, while the slopes of the fitting lines in the direct recharge zones are significantly lower than those of the meteoric water lines. The $\delta^{18}\text{O}$ - $\delta^2\text{H}$ fitting line of recharge zone E coincides with that of discharge zone E, indicating rapid karst water recharge. Moreover, $\delta^{18}\text{O}$ of karst water is relatively high

in discharge zone W, which may be attributed to the dissolution and leaching of ^{18}O from carbonate rocks.

- (3) The ^3H value of karst water increases along the flow path and it is generally higher than 9.0 TU in the discharge zones, where intensive exploitation of karst water has produced increased karst water flow in the surrounding areas, led to significant mixing between karst water receiving surface infiltration recharge and karst water receiving lateral recharge, and yielded larger changes in ^3H concentrations.

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