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Formation of the River Water Chemistry in the Middle Section of Dousitu River, China

QIAN HUI, LI PEIYUE, DING JIA, YANG CHAO and ZHANG XUEDU

School of Environmental Science and Engineering
Chang'an University, Xi'an, Shaanxi, 710054, China

qianhuixa@163.com

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Abstract: On basis of hydrogeology of the study area, the characteristics of chemistry of river water and groundwater were analyzed. Analysis results of three river water samples (B_3 , B_4 and B_5) collected in the middle section of Dousitu River show the TDS increases from B_3 to B_4 and decreases from B_4 to B_5 . The concentrations of Cl^- , Na^+ , K^+ , Mg^{2+} and HCO_3^- have a similar change with TDS, but the concentrations of Ca^{2+} and SO_4^{2-} increase steadily along flow path. The chemical types of the river water change from $HCO_3 \cdot Cl-Na$ to $Cl \cdot SO_4 \cdot HCO_3-Na$, and finally to $SO_4 \cdot Cl-Na$. The causes of these changes are analyzed and studied in depth using various methods. Results indicate river water evaporation, dissolution/precipitation of minerals, cation exchange and mixing of different waters all play important roles in the formation of the river water chemistry. But in different sections of the river, the main processes are different. The study shows that when a reservoir is built in arid areas, the loss of water resources due to evaporation is huge, which can lead to the degradation of water qualities. Hence, great care should be taken to build a reservoir in arid or semi-arid regions.

Keywords: Hydrochemistry, Evaporation, Dissolution, Precipitation, Groundwater-surface water relations, Hydrochemical modeling

Introduction

The formation of river water chemistry has always been the hot topic in hydrology and hydrogeology. It is of great importance to study the formation and evolution of river water chemistry for the purpose of river water quality protection and river ecology protection. Many hydrologists and hydrogeologists around the world have done some significant studies in this interesting and important field. Ronald J. Gibbs¹ studied the water chemistry data of the Amazon River in 1972. In his study, he recalculated the mean dissolved salts concentration. The calculated results showed that the mean dissolved salts concentration is 11 percent lower than previous calculations for South American rivers and 2.6 percent lower

than previous calculations for the rivers of the world. Rothwell *et al.*² studied the spatial and seasonal patterns of river water chemistry at approximately 800 sites in Northwest England and found that there is a clear distinction between the uplands and lowlands in water quality. Upland waters are acidic and have low concentrations of base cations, explained by background geological sources and land cover, while in the lowlands, both past and present human activities have a major impact on river water chemistry. Hein H. van Kleef *et al.*³ studied the changes caused by reduced acidifying deposition in 68 Dutch moorland pools in 2010. Smolders *et al.*⁴ revealed the intra-annual variability of the major ion composition of the Pilcomayo River, and its relationship to discharge. There are many more scientists⁵⁻⁹ paying their attention to the river chemistry study from various aspects all over the world.

Dousitu River is one of the tributaries of the Yellow River. The source of the river is near Etuok County of Inner Mongolia, China. It flows from east to west and intersects the Yellow River near Xinjian Yidui (Figure 1). The length of the river is 166 km, and the drainage area is 4160 km². The average annual¹⁰ runoff of the river is 1264×10^4 m.

Figure 1. Location of the study area and the sampling position

The Dousitu River drainage basin is situated in an arid area of north-western China. The main characteristics of the climate are a long and cold winter as well as a short and warm summer. According to the monitoring data in Etuok County, the annual temperature in the area changes from 5.3 to 8.9 °C and has an average value of 6.9 °C. The precipitation mainly occurs between June and August. The annual precipitation ranges from 125.2 mm to 611.6 mm, and has an average value of 267.5 mm. Evaporation is intensive, and the intensity is between 1947.7 and 2494.9 mm.

In the middle section of Dousitu River (B₃ to B₅ in Figure 1), the changes of the chemistry of river water are interesting. The TDS of the river water increases from B₃ to B₄, but decreases from B₄ to B₅. The concentration of Cl⁻, Na⁺, K⁺, Mg²⁺ and HCO₃⁻ has a similar change with TDS, but the concentration of Ca²⁺ and SO₄²⁻ increases steadily from B₃ to B₅. Accordingly, the chemical type of river water changes from HCO₃•Cl-Na to SO₄•Cl-Na.

What are the reasons for the changes of the chemistry of the river water? What recharge and discharge relationship between river water and groundwater can be drawn from these changes? This paper gives a detailed analysis.

Method

Geology and Hydrogeology

In recent years, much research work has been done in Ordos Cretaceous Artesian Basin (CAB)¹¹⁻¹⁴. Based on the hydrogeology, recharge and discharge characteristics of groundwater, CAB can be divided into 5 groundwater flow systems^{15,16}. Dousitu River drainage basin is one of them. According to the lithology and geological age of the strata, the aquifers in the Dousitu River drainage basin can be divided into four groups¹⁶⁻¹⁸. From the top down, they are the Cenozoic group, the Luohandong group, the Huanhe group and the Luohe group, respectively. There is no continuous aquitard between these aquifers^{18,19}.

The Cenozoic group is composed of Tertiary and Quaternary strata. The lithology of the Quaternary stratum, which covers the whole studied area, is mainly composed of fine sand of wind, flood or river deposition, with a light yellow or grey color. The lithology of the Tertiary strata is mainly sandstone and mudstone, rich in gypsum and other easily dissolving salts. It occurs primarily in the western part of the studied area (Figure 1).

The Luohandong group occurs mainly in the western part of the studied area (Figure 1). In most parts of the area, it is overlain by Tertiary stratum. It is a set of continental clastic rocks of early Cretaceous age. The maximum thickness of the formation in the region is more than 200 m. The lithology is primarily sandstone, coarse sandstone interbedded by fine sandstone, conglomerate, and sandy gravel.

The Huanhe group exists in the whole studied area (Figure 1). In the eastern part, apart from a few outcrops, the group is overlain by Quaternary stratum. In the western part, the Huanhe group is overlain by the Luohandong group. The Huanhe group is also a set of continental clastic rock formed in the early Cretaceous period. The maximum thickness of the group in the region is more than 500 m. The lithology is primarily conglomerate, sandy gravel, sandstone and becomes finer downward.

The Luohe group does not outcrop in the studied area. It is overlain by the Huanhe group in the whole region. The lithology of the group is mainly continental clastic rock of sandstone, mudstone, conglomerate and sandy gravel formed in the early Cretaceous period. The maximum thickness of the group in the region is more than 300 m.

In the Dousitu River drainage basin, groundwater is mainly recharged by precipitation. In the horizontal direction, the groundwater in all the aquifers of the north bank flows from north-east to south-west, and the groundwater in all the aquifers of south bank flows from south-east to north-west²⁰. In the vertical direction, the level of shallow groundwater in eastern part of the study area is higher than that of deep groundwater, so the water flows downward, whereas the level of deep groundwater in the western part of the study area is higher than that of shallow groundwater and the water flows upward. The discharge of groundwater in the region is mainly to the Dousitu River, pumping for irrigation, and drinking as well as the outflow to western boundary.

Chemical characteristics of river water and groundwater

To study the chemistry of river water and groundwater, 22 water samples including 5 river water samples and 17 groundwater samples were collected (in September 2004) for chemical analysis. Table 1 lists the chemical analysis results. In the table, G₁~G₁₇ are groundwater, B₁~B₅ are river water. SI_{cal}, SI_{gyp}, and SI_{dol} are the saturation indices of calcite, gypsum and dolomite, respectively.

Table 1. Chemical analysis results of Dousitu river water and nearby groundwater (Unit: mg/L)

Sample No.	Aquifer	TDS	pH	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻	SI _{cal}	SI _{dol}	SI _{gyp}
G ₁	Huanhe	327.53	7.7	23.11		60.96	25.34	42.79	35.54	155.05	0	-0.019	-0.381	-2.044
G ₂	Huanhe	629.77	8.025	130.23		47.095	26.745	40.415	44.43	358.475	0	0.526	0.843	-2.114
G ₃	Huanhe	592.56	7.6	125.2		44.1	29.2	39	76.8	341.7	0	0.034	-0.075	-1.91
G ₄	Huanhe	524.36	7.7	184		15.03	4.38	145	95.1	161.7	0	-0.636	-1.771	-2.233
B ₁	River	606.07	8.3	190	3.65	21	17.1	83.6	95.6	357	6	0.441	0.828	-2.14
B ₂	River	619.18	8.4	190	4.55	26.1	8.3	99.3	121.5	308.1	9	0.574	0.685	-1.939
G ₅	Huanhe	362.15	7.7	99.8		21.4	12.3	44	59.6	222.1	0	-0.318	-0.842	-2.248
G ₆	Huanhe	268.17	7.4	22.5		52.1	5.5	16	40.8	115.9	0	-0.5	-1.942	-1.982
G ₇	Huanhe	384.71	8.4	83.62		36.37	19.5	62.47	64.22	158.83	6.24	0.481	0.729	-2.015
G ₈	Huanhe	243.57	8.8	95.6		2.81	0.36	32.98	40.83	129.97	12	-0.254	-1.364	-3.224
B ₃	River	755.12	8.4	250	5.45	22	13.1	122.3	145.5	363.1	12	0.547	0.905	-1.974
G ₉	Cenozoic	461.62	7.6	77.17		21.91	56.97	47.03	55.83	405.42	0	-0.198	0.055	-2.368
G ₁₀	Huanhe	566.53	7.6	189		16.89	13.84	109.92	132.56	206.64	0	-0.603	-1.259	-2.072
G ₁₁	Huanhe	525.02	8.85	170.4		16.5	0	80.7	205.3	98.55	3.6	0.334	-8.519	-1.884
G ₁₂	Luohe	905.74	8.1	244.8		61.1	0.6	76.2	492.8	59.8	0	-0.156	-2.295	-1.067
B ₄	River	2922.74	8.3	1010	18.5	26.1	47.1	616.8	734.9	912.2	9	0.699	1.69	-1.532
G ₁₃	Luohandong	576.13	8	93.45		72.37	29.67	160.33	136.25	168.12	0	0.334	0.318	-1.483
G ₁₄	Luohandong	2656.725	7.87	856.755		54.91	100.4	722.355	546.195	554.34	0	0.403	1.11	-1.315
G ₁₅	Luohandong	748.345	7.92	213.24		17.535	24.31	148.015	199.815	226.675	0	-0.249	-0.322	-1.935
G ₁₆	Huanhe	703.17	7.5	146.23		51.04	36.56	129.16	140.11	203.8	0	-0.257	-0.622	-1.627
G ₁₇	Huanhe	1095.4	8	273.01		70.41	46.29	379.48	184.51	283.4	0	0.484	0.825	-1.47
B ₅	River	1854.52	8.1	535	3.65	66.1	15.6	352.7	780.5	170.9	3	0.247	-0.104	-0.987

The sampling location of these water samples is shown in Figure 1. The water samples in Table 1 are put along the flow direction. For example, the water samples before B₁ in Table 1 are in the upper part of B₁, the water samples between B₂ and B₃ are in the upper part of B₃ and lower part of B₂.

Figure 2 shows the changes of TDS and concentrations of major species in river water along the flow path. It can be seen from the figure that the TDS and the concentrations of major species in river water remain basically unchanged from B₁ to B₃. From B₃ to B₄, except the concentration of Ca²⁺, TDS and concentrations of other species increase greatly. From B₄ to B₅, except the concentrations of Ca²⁺ and SO₄²⁻, TDS and concentrations of other species decrease to some extent.

Figure 2. Changes of TDS and concentrations of major species along flow path

Figure 3 shows the changes of concentration of major cations and anions in meq% along the flow path. Similarly, from B₁ to B₃, the concentration of all the species in meq% is relatively steady. The concentration of Na⁺ in meq% is greater than 75% for all the river waters and is obviously the primary species of all the cations. By contrast, the changes of the concentration of anions in meq% are relatively large. From B₁ to B₅, HCO₃⁻ in meq% decreases while Cl⁻ and SO₄²⁻ in meq% increase. The main anion in B₁, B₂ and B₃ is HCO₃⁻, Cl⁻ and SO₄²⁻ rank second and third respectively. From B₄ to B₅, the main anions change from HCO₃⁻ to Cl⁻ and SO₄²⁻. So the chemical type of river water in B₁, B₂, and B₃ is HCO₃⁻-Na or HCO₃•Cl-Na, in B₄ it changes to Cl•SO₄•HCO₃-Na, in B₅, it becomes SO₄•Cl-Na.

Figure 3. Changes of concentration of major species in meq% along flow path

Figure 4 shows the changes of the saturation indices of calcite, dolomite and gypsum along the flow direction. It can be seen that all the river waters is undersaturated with respect to gypsum, although its saturation index increases steadily along the flow path. For calcite and dolomite, except dolomite is slightly undersaturated in B₅, all the other river waters are supersaturated with respect to the minerals.

Figure 4. Changes of saturation indices of major minerals along flow path

Figure 5 is the Piper diagram for all the waters samples in the study area, it is obvious that groundwater is mainly $\text{HCO}_3\text{-Cl-Na}$ (Ca, Mg), except G₁₁ and G₁₂ are $\text{SO}_4\text{-Cl-Na}$, and $\text{SO}_4\text{-Na-Ca}$, respectively. The TDS of groundwater has an increasing trend from the upper reaches to the lower reaches. As has been said before, in the upper reaches, the river water is mainly $\text{HCO}_3\text{-Cl-Na}$, towards the lower reaches, it changes to $\text{Cl-SO}_4\text{-HCO}_3\text{-Na}$ and $\text{SO}_4\text{-Cl-Na}$.

Figure 5. Piper diagram for the water samples in the study area

▲ Groundwater ● River water

From the above discussion we know the major changes of the chemistry of river water occurred between B_3 to B_5 , which is in the middle section of the Dousitu River. So the river in this section is divided into two parts for the study, which are B_3 - B_4 and B_4 - B_5 , respectively.

Water chemistry changes from B_3 to B_4

From B_3 to B_4 , the TDS and concentration of major species in river water increase to different degrees. According to field investigation, a dam was built in B_4 in 1978. Though the dam is only 20 m high, it forms an open water surface of about 4.5 km^2 . The direct result is the intensive evaporation of river water. Furthermore, the samples collected on 8~9 September, 2004 has experienced intensive evaporation during the whole summer. So the increase of TDS and concentration in B_4 is understandable. Further analysis of the chemistry of river water from B_3 to B_4 indicates the increase is different for different species. The concentrations of Cl^- , SO_4^{2-} , Na^+ , Mg^{2+} , K^+ and TDS in B_4 are 5.04, 5.05, 4.04, 3.6, 3.39 and 3.87 times of that in B_3 , respectively. While the increases of Ca^{2+} and HCO_3^- are relatively small, and their concentrations in B_4 are only 1.19 and 2.51 times of that in B_3 .

The river water in B_4 is mainly recharged by upstream river water and groundwater. Because the chemistry of river water and groundwater in the upper part of B_4 are similar, the river water in B_3 is used as the recharging water to analyze the formation of the chemistry of river water in B_4 .

Estimation of evaporation proportion

If there were no effects of chemical reactions, the increase rate of the concentrations of various species should be same under the sole influence of evaporation. The above-mentioned different concentration increase rates for different species indicates the formation of the river water chemistry in B_4 has been affected by some chemical reactions. For the following reasons, the main reactions are the dissolution of gypsum and halite, as well as the precipitation of calcite.

- (1) The study area is located in the arid region, the Tertiary stratum scattered in the area contains large amount of gypsum and halite. The river water in the area is all undersaturated with respect to these minerals.
- (2) River water in B_3 and B_4 is supersaturated with respect to calcite, and the concentration increase rates of Ca^{2+} and HCO_3^- are apparently smaller than that of Cl^- , SO_4^{2-} , Na^+ , Mg^{2+} and K^+ . Where have the Ca^{2+} and HCO_3^- gone during the process of evaporation? Precipitation of calcite is the natural answer.

To estimate the evaporation proportion during the formation of river water chemistry in B_4 , the effects of chemical reactions to the changes of the concentrations of various species should be analyzed first. Because of the dissolution of halite, the concentrations of Cl^- and Na^+ will increase on the basis of evaporation. So under the sole influence of evaporation, the concentration increase rates of Cl^- and Na^+ from B_3 to B_4 should be smaller than the present values of 5.04 and 4.04. In other words, evaporation proportion estimated by the concentration increase rates of Cl^- and Na^+ will be larger than the real value, although we do not know this value up to now. Because of the dissolution of gypsum, evaporation proportion estimated by the concentration increase rate of SO_4^{2-} will also be too large. Compared with the above species, estimates based on the increase rates of Ca^{2+} and HCO_3^- (1.19 and 2.51, respectively) are smaller than the real value because of the precipitation of calcite. Since the precipitation of calcite is mainly caused by the dissolution of gypsum, the contribution of dissolution of gypsum and halite to the increase of TDS is larger than the decrease caused by the precipitation of calcite. Therefore the evaporation proportion estimated by the increase rate of TDS (3.87) is also larger than the real value. Through the above

analysis, the increase rate caused solely by evaporation should be in the range of 2.51 to 3.87. Considering the increase rates of Mg^{2+} and K^+ (3.6 and 3.39, respectively), the average value of their increase rates is used to estimate the effects of sole evaporation. That is to say, in the process of formation of the chemistry of river water from B_3 to B_4 , the concentration increase rate caused solely by evaporation is 3.5, or the evaporation proportion in B_4 is 71.43%.

Reactions forming the chemistry of river water in B_4

The chemistry of river water in B_3 , B_4 and the residual water after evaporation (WAE) by the above proportion are compared in Table 2. It is clear although the chemistry of WAE is close to the river water in B_4 , but the two have distinct differences. These differences are mainly caused by chemical reactions. According to the saturation indices in Figure 4, halite and gypsum are under saturated in B_3 and B_4 , while calcite is supersaturated. So the main reactions forming the chemistry of B_4 are thought to be the dissolution of halite and gypsum, the precipitation of calcite and degassing of CO_2 , the later is the common reaction accompanying the precipitation of calcite.

Table 2 Comparison of the water chemistry of B_4 , B_3 and WAE (Unit: mg/L)

No.	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}
B_3	755.12	250	5.45	22	13.1	122.3	145.5	363.1	12
WAE	2642.92	875	19.08	77	45.85	428.05	509.25	1270.85	42
B_4	2922.74	1010	18.50	26.1	47.1	616.8	734.9	912.2	9

At the same time, because the dissolution of halite can not solely explain the increase of Na^+ in B_4 and the concentration of Mg^{2+} increased in B_4 compared with B_3 . Considering the flow rate of river water decreased a lot in B_4 because of the building of the reservoir and a thick layer of fine deposits formed in the reservoir bottom. So the above changes of the cation concentration are explained by the following reactions.

The method of mass balance is used to calculate the amount of chemical reactions (1) ~ (7) during the formation of the chemistry of river water in B_4 from WAE. Table 3 lists the calculated results. In the table, the amounts of chemical reactions (5) ~ (7) are denoted by adsorbed amount of K^+ , Ca^{2+} and Ca^{2+} , respectively. The calculated results in Table 3 confirmed the qualitative guess. That is during the formation of chemistry of river water in B_4 from WAE, the dissolution of halite and gypsum, the precipitation of calcite and the degassing of CO_2 are the main reactions. Cation exchanges between K^+ and Na^+ , Ca^{2+} and Na^+ and Ca^{2+} and Mg^{2+} also play certain roles.

Table 3. Results of chemical reactions in B_4 from WAE (Unit: mmol/L)

(1)	(2)	(3)	(4)	(5)	(6)	(7)
5.39	2.35	-3.33	-3.09	-0.01 (K^+)	-0.24 (Ca^{2+})	-0.05 (Ca^{2+})

In fact, during the processes of the formation of the chemistry of river water in B_4 , mineral dissolution and precipitation, cation exchange and evaporation occur at the same time. But evaporation is the main process, which caused the subsequent chemical reactions. The two is separated for the convenience of analysis in our discussion.

Water chemistry changes from B_4 to B_5

The changes of the concentrations of major ions with TDS for B_4 , B_5 and the groundwater between them are shown in Figure 6. It can be seen clearly from the figure that for the non-reactive ions such as Cl^- and $\text{Na}^+ + \text{K}^+$, the chemistry of river water in B_5 can be formed by the mixing of B_4 with G_{15} or G_{16} , which are the ground waters near the south and north banks of Dousitu river respectively. But for the reactive species such as Ca^{2+} , HCO_3^- , Mg^{2+} and SO_4^{2-} , the relationships between their concentrations and TDS are irregular and can not be explained by the sole process of mixing. This indicates except mixing, these species have experienced some chemical reactions which makes their TDS-concentration relation orderless. Therefore, the key questions in explaining the chemistry of river water from B_4 to B_5 are: (1) calculation of the mixing proportion between B_4 and groundwater, (2) determination of the chemical reactions from B_4 to B_5 on the basis of above mixing.

Figure 6. The relation between TDS and the concentrations of major ions

Calculation of mixing proportion

Now that the chemistry of river water in B_5 is formed by both the processes of mixing and chemical reactions, and the chemical reactions affect little to the concentration of Cl^- . So the mass balance of Cl^- is used to calculate the mixing proportion. Let p represent the mixing proportion of groundwater in river water from B_4 to B_5 , then

$$\text{Cl}_{B_5} = p \times \text{Cl}_G + (1 - p) \times \text{Cl}_{B_4} \quad (8)$$

Where, Cl_{B_4} and Cl_{B_5} represent the Cl^- concentration of river water in B_4 and B_5 , Cl_G represents the Cl^- concentration of groundwater. Using the Cl^- concentration of groundwater

G₁₅, G₁₆ and their average value, the mixing proportion of groundwater in river water from B₄ to B₅ can be calculated by equation (8). Table 4 lists the calculated mixing proportion and the corresponding composition of simply-mixed water. In the table, row B₄-G₁₅, B₄-G₁₆ and B₄-G_{avg} are the mixed results of B₄ with G₁₅, G₁₆, and G_{avg}, respectively. One thing should be noted is that G_{avg} is the simple half-and-half mixing of G₁₅ and G₁₆.

Table 4. Calculated mixing proportion and the corresponding concentrations of mixed waters (unit: mg/L)

No.	P, %	TDS	Cl ⁻	Na ⁺ +K ⁺	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	HCO ₃ ⁻
B ₄		2922.74	616.80	1028.50	26.10	47.10	734.90	912.20
B ₄ -G ₁₅	56.337	1697.75	352.70	561.13	21.27	34.26	433.45	526.00
B ₄ -G ₁₆	54.158	1720.67	352.70	542.20	39.61	41.39	412.77	528.54
B ₄ -G _{avg}	55.226	1709.43	352.70	551.48	30.62	37.90	422.91	527.30
B ₅		1854.52	352.7	538.65	66.10	15.60	780.50	170.90

Table 4 shows when the mixing proportion based on mass balance of Cl⁻ is used, the calculated concentration of Na⁺+K⁺ for the 3 sets of mixed water equals approximately to that of river water in B₅. This is because the property of Na⁺+K⁺ is similar to Cl⁻ and they all belong to the relatively non-reactive ions. But for the reactive species of Ca²⁺, Mg²⁺, SO₄²⁻ and HCO₃⁻, it is obviously improper to explain the chemistry of river water in B₅ only by the simple process of mixing. Considering the hydrogeology and calculated saturation indices of minerals, the deviations between the simply-mixed water and B₅ will be explained by the dissolution of gypsum and the precipitation of calcite and dolomite.

Dissolution of gypsum

According to the calculated results in Table 4, the concentration of SO₄²⁻ in B₅ should be 412.77~433.45 mg/L, if it were formed by the simple mixing. The actual concentration of SO₄²⁻ in B₅ is 780.5 mg/L. Since the river water in B₄, B₅ and the groundwater between them are all undersaturated with respect to gypsum (Table 1) and the Cenozoic group in the area is rich in gypsum, it is reasonable to think the extra SO₄²⁻ comes from the dissolution of gypsum through the following reaction:

Using the calculated results in Table 4, when the amounts of gypsum dissolved by the mixed water B₄-G₁₅, B₄-G₁₆ and B₄-G_{avg} are 3.615 (= (780.5-433.45)/96), 3.831 and 3.725 mmol/L, respectively, the final results will be the concentration of SO₄²⁻ in B₅.

Precipitation of calcite and dolomite

The dissolution of gypsum introduced Ca²⁺ into the water, for the mixed water B₄-G₁₅, B₄-G₁₆ and B₄-G_{avg}, the introduced Ca²⁺ are 144.60 (=3.615×40), 153.22 and 149.00 mg/L, respectively. Hence, the concentration of Ca²⁺ after mixing and dissolution of gypsum should be 165.87(=21.27+144.60), 192.83 and 179.62 mg/L, respectively. The actual concentration of Ca²⁺ in B₅ is 66.10 mg/L. The logical explanation for Ca²⁺ losses is the precipitation of calcite through the following reaction:

This is also in accordance with the calculated saturation indices of calcite in B₄ and B₅. It can be seen from equation (10) that with 1 mol precipitation of Ca²⁺, there will be 2 mol decrease of HCO₃⁻ in the solution. Therefore, for the mixed water B₄-G₁₅, B₄-G₁₆, and B₄-G_{avg}, the concentration decreases of HCO₃⁻ caused by the precipitation of calcite are 304.31 (=2×61×(165.87-66.10)/40), 386.53 and 346.22 mg/L, respectively.

At the same time, compared with 15.6 mg/L of Mg^{2+} in B_5 , the concentration of Mg^{2+} in the mixed water is obviously too large. It will precipitate by dolomite just as Ca^{2+} in the manner of calcite. Using the similar method, the concentration decrease of HCO_3^- caused by the precipitation of dolomite for the mixed water $\text{B}_4\text{-G}_{15}$, $\text{B}_4\text{-G}_{16}$ and $\text{B}_4\text{-G}_{\text{avg}}$ are 94.86 ($=2 \times 61 \times (34.26 - 15.60) / 24$), 131.10 and 113.36 mg/L, respectively.

It can be seen from the above discussion that the concentration of HCO_3^- in the mixed water of $\text{B}_4\text{-G}_{15}$, $\text{B}_4\text{-G}_{16}$ and $\text{B}_4\text{-G}_{\text{avg}}$ should be 570.07 ($170.90 + 304.31 + 94.86$), 688.53 and 630.48 mg/L, respectively if the dissolution of gypsum and the precipitation of calcite and dolomite were not happened after the mixing of B_4 with groundwater.

Restored results

In this paper, the restored concentration is defined as the concentration of mixed water without chemical reactions or before chemical reactions which can get the concentration of B_5 after the chemical reactions happens. According to the above calculation, the restored concentration of HCO_3^- is a little larger but close to the simply-mixed (Table 4). The reason for this is the precipitation of calcite may not completely follow the stoichiometric relationship of equation (10), some CO_2 produced in reaction (10) may dissolve into water and not release to the atmosphere. So the decrease of HCO_3^- calculated using the stoichiometric relationship of equation (10) may be a little larger, which leads to the larger calculated concentration of HCO_3^- .

Here the restored B_5 (represented by B_5') based on $\text{B}_4\text{-G}_{\text{avg}}$ is taken as an example to show the results. In Figure 7, the restored concentration of HCO_3^- is drawn against TDS. In this case, B_5' has already on the line drawn through G_{15} , G_{16} and B_4 , which indicates the mixing of B_4 with the average mixture of G_{15} and G_{16} can form the chemistry of river water in B_5 through the following processes: (1) mixing of 44.77% B_4 and 55.23% G_{avg} ; (2) the 3.725 mmol/L dissolution of gypsum; (3) the precipitation of calcite and dolomite by the amounts of 346.22 and 113.36 mg/L, respectively. This process also shows from B_4 to B_5 , at least 55% of river water is from groundwater.

Figure 7. The relation between TDS and the restored HCO_3^-

Conclusion

In the middle section of Dousitu River, the changes of the chemistry of river water are great. The TDS of the river water increases from B_3 to B_4 and decreases from B_4 to B_5 . The concentration of Cl^- , Na^+ , K^+ , Mg^{2+} and HCO_3^- has a similar change with TDS, but the concentration of Ca^{2+} and SO_4^{2-} increases steadily. The hydrochemical types of the river water change from $\text{HCO}_3\text{-Cl-Na}$ type to $\text{Cl-SO}_4\text{-HCO}_3\text{-Na}$ type and finally to $\text{SO}_4\text{-Cl-Na}$ type.

The chemistry of river water in B_4 is formed by the conjunctive processes of evaporation and chemical reaction. Evaporation is the main process, which makes the concentration of species increase by about 3.5 times. The main chemical reactions forming the chemistry of river water in B_4 are dissolution of halite and gypsum, the precipitation of calcite and degassing of CO_2 . Cation exchanges between $\text{K}^+\text{-Na}^+$, $\text{Ca}^{2+}\text{-Na}^+$ and $\text{Ca}^{2+}\text{-Mg}^{2+}$ also play some roles.

The concentrations of non-reactive species in B₅ can be explained by the simple mixing process. But for the reactive species, chemical reactions occurred between B₄ and B₅ have distinct effects on their concentrations. Mass balance of Cl⁻ shows the river gets more than 50% of groundwater recharge between B₄ and B₅. On the basis of mixing, the dissolution of gypsum, precipitation of calcite and dolomite and the degassing of CO₂ also play important roles in forming the chemistry of river water in B₅.

The formation processes of the chemistry of river water in B₄ indicate that when a reservoir is built in an arid area, the loss of water resources due to evaporation is huge, and making things worse, the evaporation can also lead to the degradation of water qualities. Hence, great care should be taken to build a reservoir in arid and semi-arid regions.

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