



Formation Mechanism of Water Chemical Compositions in the Lower Reaches of Dusitu River, China

H.B. ZHANG*, H. QIAN, P.Y. LI and J.H. WU

School of Environmental Science and Engineering, Changan University, Yanta Road, Xi'an, P.R. China

*Corresponding author: Fax: +86 29 82339952; Tel: +86 29 82339327; E-mail: hbzhang@chd.edu.cn

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The objective of this paper is to find out the factors causing river water chemical compositions changes in the lower reaches of Dusitu river. River water samples and groundwater samples were collected and analyzed for chemical and isotopic indices. The relationships between water chemical characteristics and geological situation, river flow and hydrogeology conditions were discussed in the study. The results show that: (1) the river flow increases firstly and then decreases along flow path, (2) the $\delta^{18}\text{O}$ and δD in river water decrease in certain degree with flow growth, but increase significantly with flow decreasing, (3) the TDS change and content change of each component increase along flow direction in the same flow, but more stable than the above parameters, (4) the corresponding hydrochemistry types of river water change from $\text{Cl}\text{-SO}_4\text{-Na}$ to $\text{SO}_4\text{-Cl-Na}$ influenced strongly by the changes mentioned before. Based on these understanding, we divided the middle and lower Dusitu River into three sub-reaches. This paper discussed the formation mechanisms of river water chemical compositions on every reach by mass balance model, saturation index and isotope fractionation. It is concluded that the formation mechanism on river water chemical composition is in difference each other taken from different reaches in Dusitu river. In its middle reach, the mixing process between river water and groundwater, dissolution of gypsum and halite and the precipitation of calcite play major roles in chemical composition forming process. In the lower river, evaporation, concentration and mixing action are the key factors to impact the formation mechanism, especially evaporation, its proportion obtained about 28.05 % according to the calculated result from isotopic data.

Key Words: Hydrogeochemistry, Dusitu river, Mixing action, Dissolution precipitation, Evaporation concentration, Formation mechanism.

INTRODUCTION

The formation process of river water chemistry has always been a hot topic in hydrology and hydrogeology field. Many hydrologists and hydro-geologists have done a lot of effective work on the formation and evolution of river water chemistry and are in contribution to water environment recovery and river ecology protection around the world. Gibbs¹ studied the water chemistry characteristics of the Amazon river and found out the rule of chemical composition change with the seasonal cycle. Edet *et al.*² analyzed the sources of water chemical constituents in the aquifer of the coastal plain and put forward a theory that natural geochemical actions and tidal motion in the estuary have conclusive effects on groundwater chemical composition change. Adams *et al.*³ applied some methods including correlate analysis and factor analysis theory to analyze water chemistry characteristics in a certain area aquifer and concluded lixiviation reaction, evaporation, concentration and interchange reaction are the main factors to form the areal characteristics. Rothwell *et al.*⁴ studied the spatial and seasonal

patterns of river water chemistry 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. Smolders *et al.*⁵ revealed the intra-annual variability of the major ion composition of the Pilcomayo river and its relationship with discharge. It was put forward that halite dissolution play an important role. Furthermore, there are many more scientists⁶⁻¹⁶ paying their attention to the river chemistry study from various aspects all over the world.

EXPERIMENTAL

Study area: Dousitu river, originated nearby Etooke County in Inner Mongolia, China, is one of the tributaries of the Yellow river. It flows from east to west, with a total length of 166 km with a drainage area of 4160 km² and intersects the Yellow river near Xinjian Yidui (Fig. 1). The average annual runoff of the river is $1264 \times 10^4 \text{ m}^3$ and the maximum runoff

is 191 m³/s. Dusitu river lies in the hinterland of the Eurasian continent, controlled by a typical continental monsoon climate with a long and cold winter and a short and warm summer. In the area, the multiyear average precipitation is 267.5 mm concentrated mainly in monsoon period. Intensive evaporation is another typical characteristic with mean annual evaporation between 2453.6-2921.6 mm.

Middle and lower reaches of Dusitu river is located to the east of Bulongmiao (Fig. 1). Based on sample analysis result in Sep 2004, it can be found that TDS reduces sharply along the flow path from 1.85 g/L to 6.06 g/L. Accordingly, the contents of major ions increase steadily. The hydro-chemical type of river water changes from Cl·SO₄-Na type in middle reaches of Dusitu river to SO₄-Cl-Na in the lower reaches. All these changes interest us to find out the causes. In this study, hydrogeochemical theory is used to analyze this problem in depth, which will be helpful for dealing with similar problems in other areas.

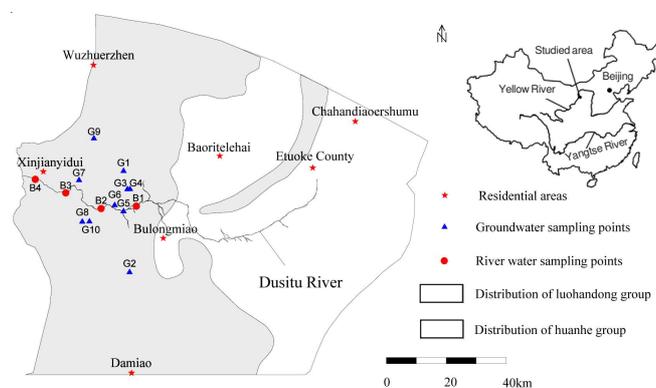


Fig. 1. Location of the study area and sampling positions

Geological and hydrogeological conditions of study area:

In the past few years, many researchers have done a lot of productive work in Ordos Cretaceous Artesian Basin (CAB)⁸⁻¹⁰. An agreement is reached that by means of analyzing the hydrogeological characteristics and recharge and discharge between river and groundwater, Cretaceous Artesian Basin can be divided into 5 groundwater systems and the Dousitu river basin is one system. According to the existing research results, its aquifers include four groups¹⁰. From the top downwards, they are the Cenozoic group, Luohandong group, Huanhe group and Luohe group. There is no continuous aquitard between two adjacent aquifers^{11,12}.

The Cenozoic group is an aquifer made up of tertiary and quaternary stratum. The quaternary stratum, composed of fine silt, silty clay and silt soil, covers the whole study area. The tertiary stratum is below the quaternary stratum and it mainly is composed of sandstone, siltstone, mudstone and gravel. It's being rich in gypsum has lead to poor groundwater quality in the aquifer. The Cenozoic group is located in the western of survey zone, mostly overlapping the distribute zone of Luohandong group. The studied lower Dusitu river is in this overlapping area (Fig. 1).

The Luohandong group exists mainly in the western part of the study area (Fig. 1). In most parts of the area, it is overlain by tertiary stratum. It is a set of continental clastic sedimentary rocks with a thickness of 200-562 mm formed in early

cretaceous age and its lithology primarily consist of sandstone and coarse sandstone.

The Huanhe group exists in the whole study area and covered by the above two groups (Fig. 1). The group is made up of Huachi stratum and Huanhe group stratum with a lithology of conglomerate and sandy-conglomerate. It mainly appeared in the upper river with its thickness of 281-768 m, whose clastic rock granularity has a tapering trend from above to below. It is the main confined water aquifer in study zone.

The Luohe group does not outcrop in the survey area. It is overlain by the Huanhe group in the whole region. The lithology mainly includes sandstone, pack-sand and conglomerate. Its maximum thickness is more than 390 m in the area.

In the Dousitu river drainage basin, groundwater is the main recharge source to the river. Its flowing direction is north-east to south-west in the northern region and from south-east to north-west in the southern area. Vertically, the water level of shallow groundwater in the eastern part of the study area is higher than that of deep groundwater, so the water flowing is from the top down. While in the western zone, the water level of deep groundwater is higher than that of shallow groundwater and the groundwater flows upward. The discharge of groundwater system in the region mainly includes such three ways as flowing to the Dousitu river, artificial pumping for irrigation and drinking outflowing across the western boundary.

RESULTS AND DISCUSSION

In this study, 14 water samples including 4 river water samples and 10 groundwater samples were collected from the middle and lower reaches of Dusitu river in Sep 2004 for chemical and isotopic analysis. At the same time, the discharge at sampling points was also measured. All sampling positions are shown in Fig. 1, the discharge and isotopic analysis results are listed in Table-1 and chemical analysis results are listed in Table-2. In the Tables 1 and 2, G1-G10 are groundwater samples, B1-B4 are river water samples, SI_{cal}, SI_{gyp} and SI_{dol} denote the saturation index of calcite, gypsum and dolomite respectively, which are calculated by the following equation from the proposed method by Crerar⁶ and Qian *et al.*¹³.

$$SI = \log \frac{IAP}{K} \quad (1)$$

where SI is the saturation indices of different minerals, K is the equilibrium constant of mineral dissolution and IAP is the activity product of major ions in mineral dissolution reaction. In using process, SI > 0 indicates this mineral is in supersaturation state relative to water solution, SI < 0 indicates that it is undersaturated relative to water solution and SI = 0 presents it is in equilibrium with water solution.

TABLE-1
DISCHARGE AND ISOTOPIC COMPOSITIONS ON
DIFFERENT SECTIONS IN THE DUSITU RIVER

No.	B1	B2	B3	B4
Q (L/s)	46.3	106	1.64	6.85
δ ¹⁸ O (‰)	-6.9	-7	-3.6	-7.6
δD (‰)	-70	-70	-54	-60

TABLE-2
CHEMICAL ANALYSIS ON RIVER WATER SAMPLES AND GROUND WATER SAMPLES (UNIT: mg/L)

No.	Aquifers	TDS	pH	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻	SI _{cal}	SI _{dol}	SI _{gyp}
B1	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
G1	Cenozoic	1466.47	8.2	460.97	460.97	29.7	38.2	436.06	340.63	321.82		0.326	0.798	-1.622
G2	Cenozoic	2447.32	7.9	666	666	72.1	93.6	586.6	854.9	256.3	0	0.21	0.568	-1.001
G3	Luohandong	839.79	7.8	235.2	235.2	23	26.8	226.9	201.7	207.5	0	-0.303	-0.505	-1.834
G4	Luohandong	1325.05	7.785	392.03	392.03	39.08	27.045	421.89	333.58	180.61	0	-0.207	-0.538	-1.478
G5	Luohandong	1753.23	7.7	522.7	522.7	35.47	46.82	493.99	579.24	144.01		-0.491	-0.826	-1.367
G6	Luohandong	1883.51	7.6	603.73	603.73	36.17	25.9	543.67	592.7	137.72	0	-0.611	-1.332	-1.349
B2	River	3299.95	8.3	995	6.35	92.2	53.2	868.5	1176.7	189.2	6	0.551	0.9	-0.821
G7	Cenozoic	3103.67	7.8	357.08	357.08	387.28	167.48	302.63	1826.15	126.09		0.438	0.541	-0.098
G8	Cenozoic	2083.36	7.9	639	639	70.1	12.2	577.9	715.6	106.8	0	-0.144	-1.013	-1.009
G9	Luohandong	684.39	8.7	182.24	182.24	31.14	26.33	148.83	144.77	211.67	15.48	0.78	1.526	-1.825
G10	Luohandong	2187.55	7.3	681	681	51.5	23.59	616.24	679.15	128.14	0	-0.831	-1.967	-1.168
B3	River	3642.4	8.3	1075	7.30	104.2	63.6	868.5	1412.1	201.4	6	0.605	1.03	-0.727
B4	River	6062.03	8.3	1650	4.55	240.3	155.5	1099	2752.1	213.6	6	0.874	1.593	-0.266

It can be concluded that the river runoff varies dramatically from B1 to B2 and to B3 and has a slight rise between B3 to B4. In accordance with the above phenomenon the δ¹⁸O and δD in river water seems have insignificant relation with flow increasing, but increase significantly with flow decreasing. Because the reasons causing the changes have already been discussed in detail in previous studies¹¹⁻¹³, it will not be repeated in the current study.

Based on the result (Table-2), the changes of TDS and major ions concentrations in river water from B1 to B4 are shown in Fig. 2. As is shown in Fig. 2, except K⁺, TDS and all ions show an increase trend from B1 to B4 with different ratios. The increasing ratio for Mg²⁺ is the biggest convinced by the concentration ratio of B4 to B1 being 9.97. Ca²⁺ and SO₄²⁻ are after Mg²⁺, their increasing ratios of B4 to B1 are respectively 3.64 and 3.53. The increasing ratios for Cl⁻ and Na⁺ are respectively 3.12 and 3.08. For K⁺ and HCO₃⁻, the ratio is 1.25 and TDS is 3.27. It is significantly influenced by the increasing of Na⁺, Cl⁻ and SO₄²⁻.

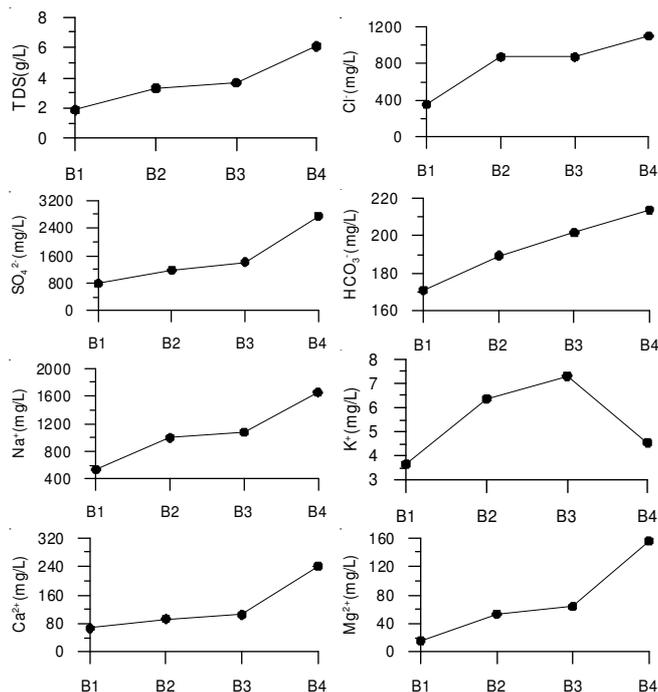


Fig. 2. Concentration variations of different cations and anions

Fig. 3 shows the variation of milliequivalent per cent (meq %) of the major cations and anions along the river flow path. It can be seen from Fig. 3 that Na⁺ is dominant among all the cations with meq % larger than 80 %. For major anions, Cl⁻ and SO₄²⁻ are dominant, but HCO₃⁻ concentration in meq % is usually less than 10 %. In the middle reaches of the river, Cl⁻ accounts for the largest percentage and SO₄²⁻ concentration gradually increases downward along river and shows a dominant state in the lower reaches. The above variations result in hydrochemical types changing from Cl-SO₄-Na in the middle to SO₄-Cl-Na in the lower reaches.

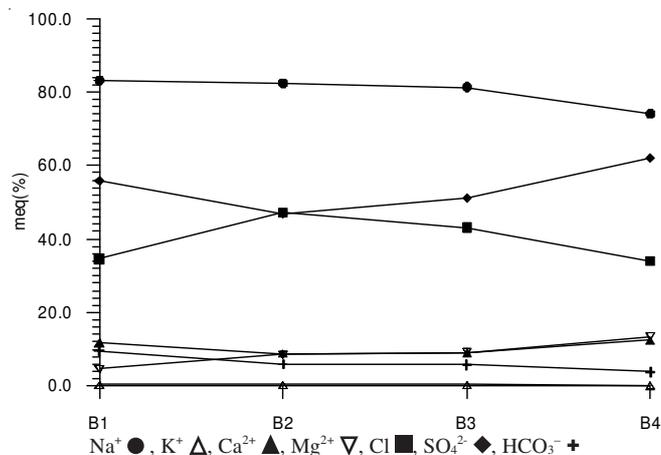


Fig. 3. Meq per cent of chemical constituent in river water along the middle and lower Dusitu river

The mineral saturation indices for calcite, gypsum and dolomite of river water taken from four sampling points are presented in Fig. 4. It demonstrates that calcite at four points is in super-saturation, gypsum is in unsaturated state and dolomite is in super-saturation except being slightly unsaturated at B1.

As stated previously, river water chemical constituents have changed dramatically along the middle and lower Dusitu river. What causes the changes and how the change rule and mechanisms impact the chemical constituents? The following sections will answer these questions.

Recently, great progress has been made in groundwater chemistry and water chemical formation mechanism. A lot of

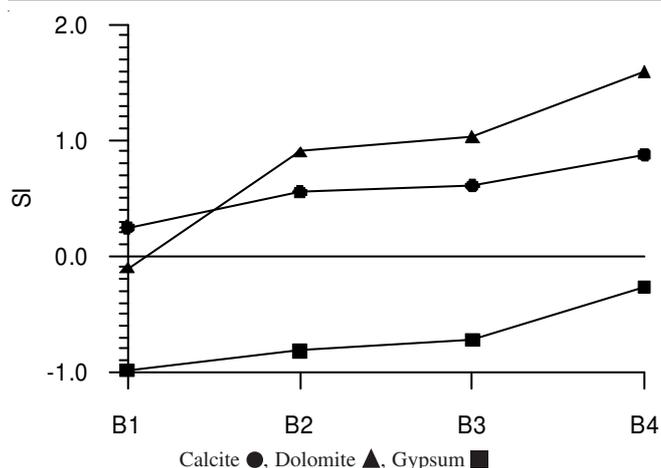


Fig. 4. Mineral saturation changes in river water on the middle and lower Dusitu river

models and programs have been developed¹⁴⁻¹⁶ and some of them have been successfully applied in solving the practical problems by many researchers¹⁷⁻¹⁹. In the paper, the authors attempt to use some hydrogeochemical methods to study the formation process of river water chemistry.

Before carrying out the work, we divided the middle and lower reaches of the river into three sub-reaches according to sampling point distribution, geological and hydro-geological conditions of the study area. Next we will respectively investigate water chemical formation mechanisms of sub-reaches.

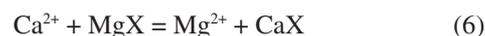
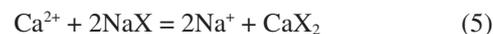
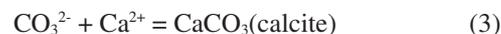
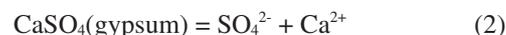
Water chemistry changes in B1-B2: The main characters for B1-B2 are: (1) river discharge increases rapidly which indicates there is a large volume of groundwater recharged into the river. (2) TDS and major ions concentrations increase to a certain extent (Fig. 2). (3) The isotopic content in river water almost is constant. According to our previous research¹⁵, it is estimated the evaporation proportion should be between 3.23 and 7.68 % in B1-B2. Hence, it can be concluded that the evaporation can hardly affect the water chemistry.

From B1 to B2, river discharge increases from 46.3 L/s to 106 L/s. Without considering the impact of evaporation, the recharge would have been 59.7 L/s, accounting for 56.32 % of the total runoff. Therefore, it can be clearly concluded that the groundwater recharge must be one of several main contributors to alternating the river water chemical constituents at B2. However, after analyzing the data in Table-2, it can be found that TDS at B2 is greater than B1 and also is greater than that of any groundwater samples between B1 and B2. Therefore, we may certain that the mixing action of groundwater and river water from the upper reach is not the only factor influencing the water chemical formations at B2. Necessarily, there must be some other chemical reactions occurring between B1 and B2 which results in TDS increasing. As the abundant soluble salt and gypsum containing in the

Cenozoic stratum in the study area are in unsaturated state relative to groundwater and surface water, it can be inferred that the dissolution of gypsum and Halite might have played an important part in forming the water chemistry.

Since there is a large volume of groundwater recharging to river water between B1 and B2, the groundwater chemical characteristics become a problem necessary to be considered before analyzing the mixing process. Six groundwater samples (G1-G6) were collected and analyzed between B1 and B2 and the average values of ions contents in the 6 samples were taken as the chemical compositions of groundwater into river. The mixing results were calculated according to the mixing ratio discussed above (56.32 %). The results are listed in Table-3. It can be seen from Table 3 that compared with the mixed water, $\text{Na}^+ + \text{K}^+$ content in B2 increase in larger amount than Cl^- , while Ca^{2+} increase in less amount than SO_4^{2-} , which is not logical for the dissolution of halite and gypsum. There seems to be two reasons explaining this phenomenon. The first reason is the increase of Ca^{2+} in water solution results in the precipitation of calcite, which can be proved by the above mentioned phenomenon of calcite being in super-saturation. Secondly, after Ca^{2+} generated from gypsum enters the water, its cation exchange with $\text{Na}^+ + \text{K}^+$ and Mg^{2+} occurs in the Cenozoic stratum, resulting in the increase of $\text{Na}^+ + \text{K}^+$ and Mg^{2+} in river water at B2.

According to the analysis, mass balance method^{20,21} is adopted to simulate the chemical reaction process between mixed water and river water at B2. The reactions are expressed as follows:



The simulated results are shown in Table-4. The simulation results show that the dissolutions of halite and gypsum, besides the mixing process, are the most important chemical reactions in the formation of river water chemical compositions. In addition, the reactions affecting the process include the cation exchange between Ca/Na and Ca/Mg, the dissolution of CO_2 and the precipitation of calcite. These reactions usually occur at the same time and for the convenience they are discussed separately in this paper.

Water chemistry changes in B2-B3: The main characteristics of river water in B2-B3 are: (1) river discharge decrease sharply from 106 L/s to 1.64 L/s (shown in Table-1). (2) TDS and major ions contents in river water increase to different degrees (Fig. 2). (3) The content of $\delta^{18}\text{O}$ and δD in river water reaches its local maximum at B3 (Table-1).

TABLE-3
COMPARISON OF MIXED WATER CHEMICAL COMPOSITION WITH OTHER RELATED WATER SAMPLE

Water sample	TDS	$\text{Na}^+ + \text{K}^+$	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}
B1	1854.52	538.65	66.10	15.60	352.70	780.50	170.90	3.00
Ground water	1652.84	488.47	43.09	39.14	437.40	526.18	202.69	0.43
Mixed water	1740.93	510.39	53.14	28.86	400.40	637.27	188.81	1.55
B2	3299.95	1001.35	92.20	53.20	868.50	1176.70	189.20	6

TABLE-4
SIMULATED RESULT OF WATER CHEMICAL REACTIONS AT B2 (UNIT: mmol/L)

Reaction (1)	Reaction (2)	Reaction (3)	Reaction (4)	Reaction (5)	Reaction (6)
13.37	5.62	-0.49	0.57	-3.14 (Ca ²⁺)	-1.01 (Ca ²⁺)

The evaporation portion was calculated using the isotopic fractionation theory. The results show the evaporation portion in the B2-B3 is 23.7-32.4 %. In this paper the average (28.05 %) is taken to discuss the impact of evaporation and concentration on river water quality.

Based on the obtained evaporation portion, the river water chemical characteristics after evaporation at B2 can be analyzed and a plot diagram showing the relationships between the results and TDS is drawn (Fig. 5). In the diagram, B2e represents the water compositions after evaporation. It can be easily seen from Fig. 5 that water chemical compositions can be obtained by simple mixing between B2e, G8 or G10. Since B2e (B2), B3, G8 and G10 plot in a line, they showing a linear relation and B3 is in the middle, so we may conclude that besides evaporation concentration, the mixing process also plays an important role in the formation of river water quality in the B2-B3.

Since mixing process is so important in influencing the chemical compositions in B2-B3, the determination of mixing proportion between B2e and G8 or G10 becomes a required question to be answered. In this paper, the mass balance of TDS among different water samples was used to calculate the mixing proportion. The mixing proportions and mixed water chemical compositions at these proportions are shown in Table-5. The water chemical characteristics at G8, G10, B3 and B2e are also listed in the table for comparison. As is shown in the table, river water at B2e mixed with groundwater at G8 at the proportion of 62.28 % or river water at B2e mixed with groundwater at G10 at the proportion of 60.64 % can both reproduce water quality at B3. Furthermore, the mixed groundwater between G8 and G10 at 1:1 can also reproduce the water chemical characteristics at B3 if mixed to river water at B2e at the proportion of 61.46 %. The mixing proportion of river water is so large at B3 and can be concluded that the maximum runoff will not occur at B2 but should appear in a position of its downstream.

Water chemistry changes in B3-B4: In B3-B4, the flow variation presents a slight increasing from 1.64 L/s at B3 to 6.85 L/s at B4 (Table-1), which means at least 76.06 % of the river runoff at B4 comes from groundwater. Based on hydrogen and oxygen stable isotopic analysis, the river water evaporation portion can be obtained¹³ as 13.7-17.9 % in B3-B4.

The chemical constituents in the river water from B3 to B4 shows a significant change. Its TDS has increased to

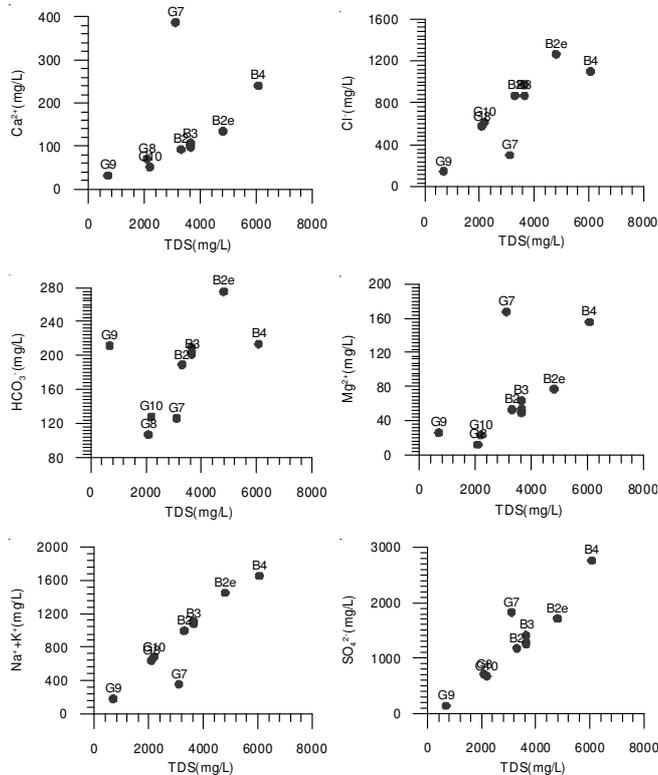


Fig. 5. Relationship between TDS and main chemical constituent in river water at B2, B3 and interval groundwater

6062.03 mg/L from 3642.4 mg/L as high as 66 % because of the great increase of SO₄²⁻ and Na⁺. Other components have weaker influence on TDS, but still show an increasing trend. Since no groundwater samples were collected between B3 and B4, the calculation to groundwater mixing proportion in the sub-reach cannot be calculated and further study on the water chemistry cannot be carried on. However, in terms of water quality change between B3 and B4, it is believed that the evaporation and concentration, mixing process, precipitation and dissolution and cation exchange perhaps may play an important role in forming the river water chemistry.

Conclusion

In this paper, based on the chemical and isotopic analysis results of river water and groundwater samples, the chemical mechanisms of Dusitu river water were comprehensively studied by the methods of mass balance, saturation index analysis and

TABLE-5
MIXING PROPORTION AND THE CORRESPONDING CONCENTRATIONS OF MIXED WATER QUALITY (UNIT: mg/L)

Water sample	TDS	Na ⁺ + K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
B2	3299.95	995.00	92.20	53.20	868.50	1176.70	189.20
B2e	4586.45	1382.90	128.14	73.94	1207.09	1635.44	262.96
G8	2083.36	639.00	70.10	12.20	577.90	715.60	106.80
G10	2187.55	681.00	51.50	23.59	616.24	679.15	128.14
B3	3642.40	1075.00	104.20	63.60	868.50	1412.10	201.40
G8-B2e (62.28 %)	3642.40	1102.34	106.25	50.65	969.79	1288.52	204.06
G10-B2e (60.64 %)	3642.40	1106.68	97.98	54.13	974.57	1259.11	209.90

isotope fractionation theory. The following conclusions are reached.

(1) TDS and major ions concentrations of river water increase steadily with the regular change of river discharge and isotopic constituents along the middle and lower reaches of Dusitu river. Influenced by these variations, the corresponding hydro-chemical type of river water changes from Cl·SO₄-Na in the middle reaches to SO₄·Cl-Na in the lower reach.

(2) The river water chemistry in B1-B2 is formed by mixing of groundwater at the ratio of 56.32 %, dissolution of halite and gypsum, cation exchange of Ca/Na and Ca/Mg, CO₂ dissolution and calcite precipitation are also important in forming the river water chemistry in B1-B2.

(3) Evaporation, concentration reaction and mixing of groundwater are important contributors to forming river water chemical constituents between B2 and B3. The related computing result shows river evaporation portion is 28.05 % and mixing portion of groundwater is in 37-40 %.

(4) In different parts of the Dusitu river, the river water chemistry is determined by different factors. In the middle reaches of the river, it is mainly controlled by the mixing process and dissolutions of halite and gypsum, while in the lower reaches, evaporation and concentration and mixing process are regarded as the most important roles.

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