

Study On Hydrogeochemical Characteristics of Deeply Buried Mining Area In Inner Mongolia - Shaanxi Province, China

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Abstract

In order to distinguish the differences of hydrogeochemical characteristics between coal measures strata and aquifers on the roof of deep buried mining areas in Inner Mongolia-Shaanxi, China, this paper adopted inorganic components, environmental isotopes and organic components to study water quality comprehensively. The results show that the deep buried mining area in Inner Mongolia-Shaanxi belongs to Mu Us Desert, and the surface is covered by aeolian sand, so it has excellent precipitation infiltration capacity. Mineralization of surface water and Quaternary water < 500mg/L, the cation is mainly Ca^{2+} , the anion is mainly HCO_3^- , which belongs to $\text{HCO}_3\text{-Ca}\cdot\text{Mg}$ type water. The Cretaceous Zhidan Group is in unconformable contact with the Quaternary, and constitutes a unified water-bearing complex on the whole, which makes Zhidan Group have a better supply water source, and its inorganic water quality characteristics are close to the Quaternary water; The deep aquifer is affected by the Anding formation relative impermeable layer and its recharge runoff condition is weak. The salinity of Jurassic water is generally > 3500mg/L due to long-term water-rock action. The cation is dominated by Na^+ and the anion is dominated by SO_4^{2-} , which belongs to $\text{SO}_4\text{-Na}$ type water. According to the analysis of hydrochemical characteristics, there is no direct hydraulic connection between Luohe Formation and Zhiluo Formation. The characteristics of environmental isotopes show that the rainwater, surface water and Quaternary water in the study area belong to the modern groundwater, while Zhidan Group water is between the modern groundwater and the ancient water. The values of δD and $\delta^{18}\text{O}$ in the deep Straight Rom Group and Yan'an Group are low, and the groundwater falls below the rainwater line of Ordos Basin with a deep circulation depth. Before mining, the groundwater is in the stagnant state with good closed conditions. The content of dissolved organic matter (TOC and UV_{254}) in groundwater decreases gradually with the increase of aquifer depth; Fluorescence peaks in Area I and Area III mainly appeared in surface water and Quaternary water, and DOM sources in surface water were more abundant; The fluorescence peak in Area I also appears in the water of Zhidan Group, Straight Rom Group and Yan'an Group, and the fluorescence peak between Area I and Area II is a symbol; The fluorescence peak intensity of Cretaceous → Straight Rom Group in Area V area has an increasing trend, indicating that there are humus like DOM from other sources in the deep Straight Rom Group aquifer. In general, the comprehensive analysis of hydrochemical characteristics by various means can well distinguish the differences of hydrogeochemical characteristics among aquifers, which provides a scientific basis for the rapid and accurate discrimination of water situation and disaster in coal mines and the safe production.

Introduction

The characteristics of China's energy endowment determine that coal is the long-term and stable main energy source in the future[1–3]. In 2020, China's coal output is as high as 3.9 billion tons, the world's largest coal production and consumer, and the absolute amount of coal production and demand in China is still on the growth trend, and the coal output will remain at about 4 billion tons during the 14th Five-Year Plan period. With the depletion of the eastern and shallow coal resources, the coal mining will extend to the deep west in the future, among which the Inner Mongolia-Shaanxi contiguous area will be the most

important. The depth of coal seams in this area is generally more than 600m[3–4], which is characterized by good coal quality[5–6] and simple geological conditions[7–8]. However, the deep-buried mining areas in Inner Mongolia-Shaanxi are newly developed mining areas, and the occurrence conditions of coal seams, roof stratigraphy structure[9] and spatial distribution characteristics of aquifers[10] are greatly changed. Moreover, the hydrogeological conditions in study area are still not fully understood[11–12], which makes it difficult to form targeted and scientific effective water prevention and control measures. Therefore, many kinds of water hazards occurred in the construction and production process of many mines[13–15], which posed a serious threat to the safe and efficient development of coal resources. A multi-layer water-rich aquifer is developed in the roof of the main coal seam in the deep-buried mining area of Inner Mongolia-Shaanxi, China. During the coal mining process, the water level of several aquifers in different mines has decreased significantly[16]. Moreover, the chemical characteristics of inorganic water in adjacent aquifers are close to each other, which makes it difficult to determine the source of underground water gushes. A large number of substances, including inorganic components, organic components and environmental isotopes, were dissolved into the groundwater during the long-term recharge and migration process[17]. Each component has its own unique migration and transformation rules, leading to significant differences in its characteristics. When distinguishing the groundwater sources of each aquifer, it can be conducted a comprehensive study on the characteristics of these components to distinguish the hydrogeochemical characteristics of each aquifer in the deep-buried mining areas of Inner Mongolia-Shaanxi, China, so as to provide a scientific basis for the identification of the source of underground inrush water.

Overview Of The Study Area

The study area is located in the eastern part of Ordos Plateau and the middle and eastern part of Mu Us Desert (**Fig.1**). The study area is generally high in the northwest and low in the southeast, with an elevation of 1300~1400m. The terrain is relatively flat, and beach and dunes are alternately distributed, mainly beach and dunes are widely distributed. The area belongs to the middle temperate zone, semi-arid to semi-arid and semi-desert monsoon climate, strong solar radiation, rich sunshine, dry and rainless, annual precipitation of 350-400mm, annual evaporation of 2200-2800mm, strong wind and sand, short frost-free period. The winter here is long and cold, summer is hot and short, and it warms up quickly in spring, the temperature drops significantly in autumn. The main rivers in the area are Wuding River, Nalin River, and the Hailiu River. Among them, Nalin River originates in the northwest of Taolisumu, Wushen Banner, flows southeast through Gujiapan Village, Nalin River Township and enters Wuding River, with a total length of about 67km, a basin area of about 1788km², an annual runoff total of 1,577 ×10⁴m³, an average flow of 0.4m³/s, and an annual sediment discharge of 153×10⁴t. It is a seasonally controlled perennial flowing river. At present, the main production mines are Nalin River No. 2, Yingpanhao, Baijiahaizi and Tahutu in the construction stage.

Hydrogeological Condition

The study area belongs to Jurassic coalfield in Ordos Basin. Yanchang Formation of the Upper Triassic is the sedimentary basement of Jurassic coal-accumulating basin and coal-bearing strata, and the Jurassic, Cretaceous and Quaternary strata are developed above Yanchang Formation (**Fig. 2**). Due to sedimentary cycle control, the middle coarse sandstone aquifer is developed in each rock section. The study area belongs to the Wulanmulun River - Wuding River groundwater flow system in the northern area of Ordos Basin. The surface is covered by aeolian sand and lacustrine sand, and the infiltration capacity of precipitation is strong, which leads to the Quaternary loose pore aquifer with good permeability and rich water content. The strata thickness of this section is 8.60~63.57m, and the unit water inflow is 0.69~3.23L/s·m. Some sections of the Salawusu Formation of the Upper Pleistocene are greater than 5.0L/s·m, and the permeability coefficient is 10.76~11.81m/d. It is a medium-strong water-rich aquifer, and the buried depth of water level is 1.0~3.0m. The Cretaceous Zhidan Group aquifer is mainly composed of fluvio-lacustrine clastic deposits, which are characterized by large thickness (generally 300 ~ 600m), interbedded structure of sand and mudstone and complex phase transition, and multi-layer aquifers are developed. The thickness of the aquifer is 53.70 ~ 335.02m, the lithologic composition and permeability vary greatly, and both the aquifer and the impermeable layer are unstable in the horizontal direction. There are hydraulic relations among the aquifers, which are closely related to the overlying Quaternary aquifers, forming a unified water-bearing complex with a unit inflow of 0.22~ 1.46L/s·m and a permeability coefficient of 0.23~1.91m/d. It is a medium-strong water-rich aquifer. The lower lithologic assemblage of Zhiluo Formation is dominated by medium and fine-grained feldspar quartz sandstone, and the local section is very thick bedded coarse-grained feldspar sandstone. The thickness of the aquifer is 29.06 ~ 71.20m, the unit water inflow is 0.01~0.02L/s·m, the permeability coefficient is 0.02 ~ 0.07m/d, and the aquifer water abundance is weak. Yan'an Formation is the main coal-bearing strata in the study area, consisting of five coal groups: 2, 3, 4, 5 and 6. According to its sedimentary cycle and lithologic assemblage characteristics, it can be divided into three rock sections. The lithology of the aquifer is mainly gray medium and fine feldspar quartz sandstone, which is interbedded with siltstone, mudstone and sandy mudstone water-insulating layer vertically. The aquifer thickness is 34.70~71.18m, the unit water inflow is 0.04~0.12L/s·m, and the permeability coefficient is 0.08~0.14m/d. It is a weak-medium water-rich aquifer.

Sample Collection And Detection Analysis

A total of 47 groups of water samples were collected in this paper (**Table 1**), including 26 groups of inorganic total analysis, 14 groups of isotopes, and 26 groups of organic matter. Water samples were collected from the Quaternary, Cretaceous, Zhiluo, Yan'an and other aquifers.

The main detection indicators include:

(1) Total analysis: K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , NO_3^- , NO_2^- , NH_4^+ , Fe^{3+} , Fe^{2+} , pH, free carbon dioxide, total hardness, total acidity, total salinity, etc.

(2) Isotope: D ^{18}O

(3) Organics: 3DEEM□TOC□UV₂₅₄□

All the samples were filled and sealed in 2.5L plastic drums and sent to the hydrochemical analysis laboratory of Xi'an University of Science and Technology and Xi'an Research Institute of China Coal Science and Engineering Group Co., Ltd for water quality index test. Relevant maps were drawn with Corel Draw 12, and relevant data were analyzed with software such as Origin and Excel.

Table 1 Water sample basic information

Sample No.	Layer Position	Sampling point	Detection items
Rain water-1	Rain water	Rain water	Isotope
NLH	Surface water	Surface water	Total analysis
18T-55-362	Surface water	Surface water	Isotope
Pool-2	Surface water	Pool-2	Organics
T61-1	Quaternary	Quaternary	Total analysis
DSG-1	Quaternary	Quaternary	Total analysis□Isotope
DSG-1-2	Quaternary	Field 1 Quaternary	Organics
#1-2	Quaternary	Civil well□Quaternary	Organics
#1-3	Quaternary	Quaternary	Isotope
#2-2	Quaternary	Civil well□Quaternary	Organics
#3-2	Quaternary	Civil well□Quaternary	Organics
#4-2	Quaternary	Civil well□Quaternary	Organics
#5-2	Quaternary	Civil well□Quaternary	Organics
#6-2	Quaternary	Civil well□Quaternary	Organics
#7-2	Quaternary	Civil well□Quaternary	Organics
#8-2	Quaternary	Civil well□Quaternary	Organics
#9-2	Quaternary	Civil well□Quaternary	Organics
T66-1	Cretaceous system	Cretaceous system	Total analysis
ZDG-1	Cretaceous system	Cretaceous system	Total analysis
ZDG-2	Cretaceous system	Cretaceous system	Total analysis
ZDG-3	Cretaceous system	Cretaceous system	Total analysis
ZDG-4	Cretaceous system	Cretaceous system	Total analysis
ZDG-4-3	Cretaceous system	Cretaceous system	Isotope
ZDG-1-2	Zhidan group	Field 1 Zhidan group	Organics
ZDG-2-2	Zhidan group	Field 2 Zhidan group	Organics

ZDG-4-1	Zhidan group	Field 4 Zhidan group	Organics
ZDG-3-2	Zhidan group	Field 3 Zhidan group	Organics
ZLG-1-2	Straight rom group	Field 1 Straight rom group	Organics
ZLG-4-1	Straight rom group	Field 4 Straight rom group	Organics
ZLG-3-1	Straight rom group	Field 3 Straight rom group	Organics
ZLG-2-1	Straight rom group	Field 2 Straight rom group	Organics
T35-1	Straight rom group	Straight rom group	Total analysis
ZLG-1	Straight rom group	Straight rom group	Total analysis
ZLG-1-3	Straight rom group	Straight rom group	Isotope
ZLG-2	Straight rom group	Straight rom group	Total analysis
ZLG-3	Straight rom group	Straight rom group	Total analysis
ZLG-4	Straight rom group	Straight rom group	Total analysis
T38-1	Yan'an Group	Yan'an Group	Total analysis
T64-1	Yan'an Group	Yan'an Group	Total analysis
DCC-1-2	Yan'an Group	2-2 Coal seam roof section	Total analysis
DCC-2	Yan'an Group	2-2 Coal seam roof section	Total analysis
DCC-4	Yan'an Group	2-2 Coal seam roof section	Total analysis
DCC-1-2	Yan'an Group	2-2 Coal bottom-3-1 Coal bed roof	Total analysis
DCC-1-2-3 ☒1☒	Yan'an Group	2 Coal roof aquifer	Isotope
DCC-1-2-3 ☒2☒	Yan'an Group	2 coal-3 coal aquifer	Isotope
DCC-1-3	Yan'an Group	3-1 Coal bottom-4-1 Coal seam top	Total analysis
DCC-1-1	Yan'an Group	2-2 Coal seam	Total analysis
DCC-2	Yan'an Group	2-2 Coal seam	Total analysis
DCC-4	Yan'an Group	2-2 Coal seam	Total analysis
DCC-4-3	Yan'an Group	2 Coal	Isotope
DCC-2	Yan'an Group	2-2 Coal seam	Total analysis
DCC-4	Yan'an Group	2-2 Coal seam	Total analysis
DCC-2-3	Yan'an Group	Aquifer between 3 ⁻¹ coal and 4 ⁻¹ coal	Isotope

DCC-1-1	Yan'an Group	3-1 Coal seam	Total analysis
DCC-1-1-3	Yan'an Group	2 Coal☐3 Coal	Isotope
DCC-1-3-3 ☐1☐	Yan'an Group	Aquifer between 3 ⁻¹ coal and 4 ⁻¹ coal	Isotope
DCC-1-3-3 ☐2☐	Yan'an Group	Aquifer between 4 ⁻¹ coal and 4-2 coal	Isotope
DCC-3-3	Yan'an Group	3-1Coal seam	Total analysis
DCC-1-2-1	Yan'an Group	Upper DCC-1-2, Field 1 2 Coal roof aquifer	Organics
DCC-4-1	Yan'an Group	Upper DCC-1-2, Field 4☐2 Coal	Organics
DCC-1-1-1	Yan'an Group	Upper DCC-1-1, Field 1 2 Coal roof aquifer	Organics
ZLG-1-2-1	Yan'an Group	Field 1 DCC-1-2 lower Aquifer between 2 coal and 3 coal	Organics
DCC-4-2	Yan'an Group	Field 4 lower DCC-4☐2 Coal	Organics
DCC-2-1	Yan'an Group	Upper DCC-2, Field 2 2 Coal roof aquifer	Organics
DCC-1-3-1	Yan'an Group	Upper DCC-1-3, Field 1 3 - 1 to 4 - 1 aquifers	Organics
DCC-2-2	Yan'an Group	Field 2 DCC-2 lower☐2 Coal	Organics
DCC-1-1-2	Yan'an Group	Field 1 DCC-1-1 lower☐3 Coal	Organics
ZLG-1-2-1	Yan'an Group	Lower DCC-1-2, field 1 2-3 inter-coal aquifer	Organics
DCC-4-2	Yan'an Group	Field 4 Lower DCC-4☐2 Coal	Organics
DCC-2-1	Yan'an Group	Upper DCC-2, Field 2 2 Coal roof aquifer	Organics
DCC-1-3-1	Yan'an Group	Upper DCC-1-3, Field 1 3-1 to 4-1 aquifers	Organics
DCC-2-2	Yan'an Group	Field 2 Lower DCC-2☐2 Coal	Organics
DCC-1-1-2	Yan'an Group	Field 1 Lower DCC-1-1☐3 Coal	Organics

According to the established criterion of “Five Elements” hydrochemical discrimination (**Table 2**), the water sample data collected were analyzed and discriminated to screen out abnormal water samples to avoid influencing the analysis results.

Table 2 “Five Elements” hydrochemical discrimination

Level	Index/(mg•L-1)	Discriminant result		
		Normal (√)	In doubt (?)	Abnormal (×)
1	pH	7.0~8.5	8.5~9.0	>9.0
2	TDS	>3 000	2 000~3 000	<2 000
3	HCO ₃ ⁻	>100	50~100	<50
4	SO ₄ ²⁻	>2 000	1 000~2 000	<1 000
5	Ca ²⁺ , NO ₃ ²⁻ , etc.	Identification of Hydrogeochemical Characteristics in the Study Area		

Results And Discussion

Chemical characteristics of inorganic water

The formation and evolution of groundwater hydrochemical composition is a very complicated process, which is closely related to lithology, structural conditions, climate conditions, hydrodynamic conditions and other factors, and comprehensively reflects the physical and chemical results and equilibrium conditions of water-rock interaction in the process of groundwater migration. Different water bodies and aquifers have different hydrochemical characteristics due to the different properties of surrounding rock, circulation conditions, REDOX conditions and mixing, which reflect the difference of recharge, runoff and discharge conditions. Through hydrogeochemical analysis of water samples, the water cycle conditions of groundwater can be determined and the water sources of different aquifers can be judged. One of the main laws of groundwater distribution is its zonation. The zoning of groundwater is mainly manifested in hydrogeological dynamic zoning and hydrogeochemical zoning.

(1) Basic characteristics of each aquifer

Surface water: The main surface water body in the study area is Nalin River water, with a low salinity (**Fig. 3**), a concentration of 303.00mg/L and a pH of 7.50, belonging to weakly alkaline water (**Fig. 4**). The main cation is Ca²⁺ with the concentration of 49.04mg/L, followed by Mg²⁺ and Na⁺; The main anions is HCO₃⁻, with a concentration range of 218.14mg/L, followed by SO₄²⁻ and Cl⁻. The main hydrochemical type is HCO₃-Ca water (**Fig. 5**), which has the same water quality as meteoric precipitation.

Quaternary system: Because the terrain of Tahutu mine field is relatively flat, and the beach and sand dunes are distributed alternantly, the beach is the main one, and the sand dunes are widely distributed. The loose sand layer of the Quaternary system directly receives the infiltration of meteoric water, the infiltration coefficient of precipitation is 0.35~0.43, the groundwater runoff path is short, and the water cycle is positive. It is characterized by low salinity, weak alkalinity and calcium bicarbonate water. Its water quality characteristics are as follows: The pH value is 7.30 (**Fig. 4**), and the salinity is 363.72 mg/L (**Fig.3**); the main cation is Ca^{2+} , and the concentration range is 61.66 mg/L, followed by Mg^{2+} and Na^+ ; the main anion is HCO_3^- with a concentration range of 232.36 mg/L, followed by SO_4^{2-} and Cl^- ; the hydrochemical type of Quaternary water is mainly $\text{HCO}_3\text{-Ca}$ (**Fig. 5**).

Cretaceous system: The water chemical characteristics of Cretaceous Zhidan Group also show the characteristics of low salinity, weak alkalinity and calcium bicarbonate type water, and the pH value in the water sample is 7.90~7.94 (**Fig. 4**). The salinity in Zhidan Group aquifer is also low (277.00~301.87mg/L) (**Fig. 3**). The main reason is that there is no stable water barrier between Cretaceous strata and the upper Quaternary strata, so the hydraulic connection is very close and the water cycle is fast. The main cation is Ca^{2+} and Na^+ with concentrations ranging from 28.90 ~ 30.96 mg/L and 29.21 ~ 39.72 mg/L, respectively, followed by Mg^{2+} ; the main anion is HCO_3^- , with concentrations ranging from 159.80 ~ 183.16 mg/L, followed by SO_4^{2-} and Cl^- ; The hydrochemical types of the Cretaceous aquifer water are mainly $\text{HCO}_3\text{-Ca}\cdot\text{Na}$ and $\text{HCO}_3\text{-Na}\cdot\text{Ca}$ water (**Fig. 5**).

Straight Rom Group: Anding formation plays an important role in preventing the hydraulic connection between the upper and lower aquifers. With the increase of the depth of underground water, the pore and fissure development is poor, supply condition is poor, runoff condition is poor, circulation path of underground water is long, contact time with the surrounding rock is long, the space is relatively closed, and water quality renewal time is long. Under the action of long-term water and rock, water quality becomes worse and the salinity is higher. Groundwater of Zhiluo Formation is characterized by high salinity, weak alkalinity and sodium sulfate. The pH value of water sample is 7.40 (**Fig. 5**), and the salinity is 7447.44 mg/L (**Fig. 4**); the main cation was Na^+ with the concentration of 1565.50 mg/L, followed by Mg^{2+} and Ca^{2+} ; SO_4^{2-} is the main anion, with a concentration of 5001.84 mg/L, followed by HCO_3^- and Cl^- . The water chemical type of Zhiluo Formation aquifer is $\text{SO}_4\text{-Na}$ water (**Fig. 5**).

Yan'an Group: The upper strata of Yanan Formation are unconformably in contact with the strata of Straight Rom Group, and can be directly replenished by the aquifer of Straight Rom Group. The lower part is the interbedded structure of multi-layer coal seam and sand and mudstone layer, which can effectively block the infiltration and overflow of groundwater in this section, so that the hydrochemical characteristics of aquifer water in this section are very close to those of Straight Rom Group. The pH value of groundwater in Yanan Formation is 7.30~8.36 (**Fig. 4**), and the salinity is 6621.00~8962.76mg/L (**Fig. 5**); The main cation is Na^+ with the concentration of 1521.00~2601.00 mg/L, followed by Mg^{2+} and Ca^{2+} ; the main anion is SO_4^{2-} with the concentration of 4409.97~5810.06mg/L, followed by HCO_3^- and

Cl⁻. The hydrochemical type is SO₄-Na water (**Fig. 5**). The concentration of Cl⁻ ion in DCC-2-1~3 water samples is 64.50mg/L, which is significantly lower than that in other water samples (555.96~676.00mg/L), and the hydrochemical type is SO₄-Na·Ca water, indicating that there were certain anomalies in DCC-2-1~3 water samples.

(2) Comprehensive analysis of aquifer characteristics

As can be seen from Piper trilinear chart (**Fig. 5**), surface water, Quaternary water and Cretaceous water samples are all located at the left end or middle left of the rhomboid. It directly shows the water quality characteristics of HCO₃-Ca (Mg) type water, that is, the water quality type of low-salinity solution and filtration water. It represents that these aquifers (bodies) receive the replenishment of meteoric water, runoff condition is relatively good, and the cycle alternates positively. The water samples of Straight Rom Group and Yan'an Group are located at the right end of the rhomboid, which shows the water quality characteristics of SO₄-Na water, namely high salinity, large amount of Na⁺ and SO₄²⁻ ions dissolved into the water, showing obvious hydrochemical characteristics different from shallow aquifers.

Durov chart (**Fig. 6**) further shows that in surface water, Quaternary and Cretaceous groundwater, Ca²⁺ and HCO₃⁻ ion concentrations representing positive alternation of shallow water cycle are relatively high, while Cl⁻, SO₄²⁻ and Na⁺ ions representing deep retained water quality are relatively low. On the contrary, the concentration percentages of Cl⁻, SO₄²⁻ and Na⁺ in the groundwater of Straight Rom Group and Yan'an Group are significantly increased.

According to Schoeller's chart (**Fig. 7**), the hydrochemical characteristic curves of surface water, Quaternary water and Cretaceous water have roughly the same shape trend, with only slight vertical movement. It shows that the chemical composition and specific gravity of each water sample are close, and the replenishment source is the same. The hydrochemical characteristic curves of Straight Rom Group and Yan'an Group are obviously different from those of shallow aquifers, indicating that there are different sources and genesis of shallow and deep groundwater.

In addition, combined with Scatter chart (**Fig. 8**), it can be further found that each aquifer increases with the burial depth. The Ca²⁺ ion concentration is relatively low in shallow aquifers and generally high in deep aquifers. The concentration of Na⁺, Cl⁻ and SO₄²⁻ also showed a similar pattern. However, the concentration of HCO₃⁻ ion has no direct relationship with the buried depth, indicating that with the buried depth of aquifer, groundwater migration and stagnant flow conditions, and long-term water-rock interaction results in a gradual increase in the concentration of most ions.

The above rules are also clearly reflected in Ludwig Langelier chart (**Fig. 9**), that is, the concentrations of Na⁺+K⁺ and SO₄²⁻+Cl⁻ conform to the vertical zoning of hydrogeochemistry. The concentrations of Na⁺+K⁺ and SO₄²⁻+Cl⁻ gradually increase with the increase of burial depth.

According to the hydrogeological data and groundwater runoff in Taohutu mine field, surface water and Quaternary aquifer are closely related to the hydraulic power of meteoric precipitation. Its runoff is controlled by topography, the groundwater runoff path is short, and the water cycle is active, so only a small amount of minerals are dissolved in the rainfall infiltration process, and the water contains different ion components, thus forming the bicarbonate fresh water with low salinity mainly caused by leaching and filtration, and providing abundant recharge water for underlying aquifer. There is no water-barrier between Cretaceous and Quaternary, which constitutes a unified aquifer group with close hydraulic connection. As a result, the groundwater of Cretaceous aquifer also belongs to the low salinity bicarbonate fresh water. Anding formation plays an important role in preventing the hydraulic connection between the upper and lower aquifers. With the increase of the depth of underground water, the pore and fissure development is poor, supply condition is poor, runoff condition is poor, circulation path of underground water is long, contact time with the surrounding rock is long, the space is relatively closed, and water quality renewal time is long. Under the action of long-term water and rock, water quality becomes worse and the salinity is higher (**Fig. 3 and Fig. 4**). Combined with the analysis of hydrochemical characteristics, it can be seen that the change rule of total hydrochemical types from shallow aquifer to deep aquifer in Tahutu mine field is as follows: $\text{HCO}_3\text{-Ca}\cdot\text{Mg}\rightarrow\text{HCO}_3\text{-Na}\rightarrow\text{SO}_4\text{-Na}$.

Isotope hydrochemical characteristics

By using environmental isotope testing techniques to study of groundwater movement, it can quickly and effectively obtain important hydrogeological information which is difficult or impossible to obtain by other methods. Since environmental isotopes are used as natural tracers to “mark” the formation process of natural water and groundwater, it is possible to directly obtain the information of the formation and movement process of groundwater by studying their distribution in various water bodies. The approach is to reveal the origin, formation conditions, recharge mechanism and hydrodynamic relationship of groundwater by comparing the difference and variation rules of environmental isotopes between underground water and surface water through analysis of environmental isotopes. Therefore, this method has been widely used in the study of hydrogeology at home and abroad[18-20].

In order to study the source of groundwater in the Tahutu Mine Field, we gathered/collected and tested 14 groups of isotopic water samples from each aquifer (**Table 3**). As can be seen from the table, the water sample test results of DCC-1-2-3 (1) and DCC-1-3-3 (2) were abnormal, the following analysis was not included in the study.

Table 3 Environmental isotope test results

Water sample No.	Layer Position	δD	$\delta^{18}O$	Remark
Rain water-1	Rain water	-52.0	-7.9	
18T-55-362	Surface water	-49	-6.1	CY-10 Ursue Haizi
DSG-1-3	Quaternary	-63.7	-8.5	Quaternary
#1-3	Quaternary	-59.7	-8	Civil well
ZDG-4-3	Zhidan group	-70.6	-9.4	Zhidan group
ZLG-1-3	Straight rom group	-69.1	-9.4	Straight rom group
DCC-1-2-3(1)	Yan'an Group	-56.3	-7.5	2 Coal roof aquifer (abnormal)
DCC-1-2-3(2)	Yan'an Group	-90.8	-11.6	2 Coal-3 Coal aquifer
DCC-4-3	Yan'an Group	-90.9	-11.7	2 Coal
DCC-1-1-3	Yan'an Group	-88.9	-11.3	2 Coal
DCC-1-3-3(1)	Yan'an Group	-89.3	-11.4	Aquifer between 3 ⁻¹ coal and 4 ⁻¹ coal
DCC-1-1-3	Yan'an Group	-91.1	-11.2	3 Coal
DCC-2-3	Yan'an Group	-91.8	-11.3	2 Coal roof aquifer
DCC-1-3-3(2)	Yan'an Group	-63.6	-8.6	Aquifer between 4-1 coal and 4-2 coal (anomaly)

Rainwater in this area has typical modern water (groundwater) characteristics (**Fig. 10**). The surface water collected from Wusuhaizi is enriched in heavy isotopes, which indicates that surface water is affected by strong evaporation and tends to sea water distribution area.

The degree to which the water sample isotopes deviate from the rainwater line can be indicated by a surplus of deuterium ($d\delta D \approx 6.37\delta^{18}O$). $d\delta D > -3.69\text{‰}$ when δ value falls on the rainwater line, and δ value falls on the lower right side of the rainwater line, $d\delta D < -3.69\text{‰}$, while the δ value falls to the upper left of the rainwater line, $d\delta D < -3.69\text{‰}$. The number of deviation from -3.69‰ of d value is equal to the distance of water sample along the direction parallel to the δD axis in Figure 11, which can often indicate the degree of evaporation in the groundwater source area and also reflect the degree of evaporation in recharge process. The $\delta^{18}O$ value increases due to the exchange of ^{18}O isotope between groundwater and rocks, resulting in ^{18}O drift.

The environmental isotopes in the groundwater in the study area, as Quaternary \rightarrow Cretaceous \rightarrow Straight Rom Group \rightarrow Yan'an Group, are gradually migrating to the deep groundwater (**Figure 11**). In particular, the deep Straight Rom Group and Yan'an Group have low values of δD and $\delta^{18}O$, and fall below the

rainwater line of Ordos Basin, which are the groundwater with deep circulation depth and with good closed condition before mining. The lower values of δD and $\delta^{18}O$ are due to the presence or mixing of Paleo-leaching and infiltration water formed under the conditions of palaeoclimate. Paleo-leaching and infiltration water refers to the groundwater formed by the infiltration of atmospheric precipitation under the paleoclimate conditions since the Quaternary. The δD and $\delta^{18}O$ values of the paleo-groundwater formed during the glacial period are lower than those of modern water. High salinity water samples that deviate from the rainwater line and below the rainwater line are due to the occurrence of "oxygen isotope drift", which results in the increase of $\delta^{18}O$ value. Under the condition of high temperature, ^{18}O in groundwater is enriched due to the isotope exchange between $H_2^{16}O$ and ^{18}O in oxygen-bearing rocks (silicate rocks and carbonate rocks), while the δD value remains basically unchanged. On the whole, the values of environment isotopes D and ^{18}O value objectively reflect that with the increase of the depth of underground water in Tahutu mine field, the formation age of water is longer.

Organic hydrochemical characteristics

On the basis of organic geochemistry and hydrogeology, this paper studies the quantity, composition and distribution of organic materials in groundwater and their roles in geological, geochemical and other processes by using qualitative and quantitative markers of various organic components in water[21-23]. Organic hydrochemical characteristics of each aquifer in Tahutu Mine can be established by testing the organic matter of each aquifer sample (**Table 4**).

Table 4: Basic information of organic matter test of water sample

Sample No.	Sampling point position	Layer position	Sample No.	Sampling point position	Layer position
Pond-2	Pond -2	Surface water	ZDG-3-2	Field 3 Zhidan group	Zhidan group
DSG-1-2	Field 1 Quaternary	Quaternary	ZLG-1-2	Field 1 Straight rom group	Straight rom group
#1-2	Quaternary	Quaternary	ZLG-4-1	Field 4 Straight rom group	Straight rom group
#2-2	Quaternary	Quaternary	ZLG-3-1	Field 3 Straight rom group	Straight rom group
#3-2	Quaternary	Quaternary	ZLG-2-1	Field 2 Straight rom group	Straight rom group
#4-2	Quaternary	Quaternary	DCC-1-2-1	Upper DCC-1-2, Field 1 2 Coal roof aquifer	Yan'an Group
#5-2	Quaternary	Quaternary	DCC-4-1	Upper DCC-1-2, Field 4 2 Coal	Yan'an Group
#6-2	Quaternary	Quaternary	DCC-1-1-1	Upper DCC-1-1, Field 1 2 Coal roof aquifer	Yan'an Group
#7-2	Quaternary	Quaternary	ZLG-1-2-1	Field 1 DCC-1-2 lower Aquifer between 2 coal and 3 coal	Yan'an Group
#8-2	Quaternary	Quaternary	DCC-4-2	Field 4 lower DCC-4 2 Coal	Yan'an Group
#9-2	Quaternary	Quaternary	DCC-2-1	Upper DCC-2, Field 2 2 Coal roof aquifer	Yan'an Group
ZDG-1-2	Field 1 Zhidan group	Zhidan group	DCC-1-3-1	Upper DCC-1-3, Field 1 3 - 1 to 4 - 1 aquifers	Yan'an Group
ZDG-2-2	Field 2 Zhidan group	Zhidan group	DCC-2-2	Field 2 DCC-2 lower 2 Coal	Yan'an Group
ZDG-4-1	Field 4 Zhidan group	Zhidan group	DCC-1-1-2	Field 1 DCC-1-1 lower 3 Coal	Yan'an Group

Total Organic Carbon (TOC) was measured by multi N/C 2100 expert Total Organic Carbon/Total nitrogen analyzer. The water sample was filtered by 0.45µm filter membrane, and the filtrate was taken to detect

the Total Organic Carbon content. The UV absorbance (UV_{254}) was detected by Evolution 60 UV-Vis Photometer. The water sample was placed in a quartz dish of 1cm size to detect the UV absorption value (UV_{254}) at 254nm, and calibration with blank water sample.

According to the detection of TOC and UV_{254} in each aquifer (**Fig. 12**): in surface water, $C(\text{TOC})= 3.484 \text{ mg/L}$, $C(UV_{254})= 0.064 \text{ cm}^{-1}$. The organic matter content in the water is low, which is similar to the situation in Nalin River No.2, Hongqing River, Balasu and other mines in this area, indicating that the nitrogen and organic content of industrial and agricultural pollution sources in this region is very low, and the surface vegetation is sparse. In Quaternary water, $C(\text{TOC})= 0.345\sim 1.344 \text{ mg/L}$, $C(UV_{254})= 0.005\sim 0.026 \text{ cm}^{-1}$, and Dissolved Organic Matter (DOM) concentration is low. The main reason is that the organic matter in surface water and aerated zone water enters Quaternary system and reacts further with DO , NO_3 and other electron donors. The same characteristics are also shown in the Zhidan Group aquifer water, $C(\text{TOC})= 0.452\sim 1.076 \text{ mg/L}$, $C(UV_{254})= 0.004\sim 0.029 \text{ cm}^{-1}$, it is possible that Fe and Mn are involved in the reaction, and organic matter is the carbon source. In deep Zhiluo Formation aquifer water, $C(\text{TOC})= 0.5352\sim 1.471 \text{ mg/L}$, $C(UV_{254})= 0.002\sim 0.009 \text{ cm}^{-1}$. The organic matter concentration in the deep aquifer of Yanan Formation varies greatly, which may be affected by coal measure strata, $C(\text{TOC})= 0.329\sim 3.943 \text{ mg/L}$, $C(UV_{254})= 0.0004\sim 0.075 \text{ cm}^{-1}$.

In general, DOM concentration decreases with the increase of buried depth of aquifer (from surface water \rightarrow Quaternary \rightarrow Cretaceous \rightarrow Straight Rom Group). The REDOX reaction of these substances with DO and NO_3 in the process of migration with groundwater is the main factor leading to the decrease of content. TOC concentration in the water of Yanan Formation varies greatly, which may be influenced by the coal-bearing strata.

The characteristics of fluorescence spectrum distribution of dissolved organic matter vary with the types and contents of organic matter, and are corresponding to the characteristics of water samples, which are called "fluorescence fingerprints"[24-26]. Three-dimensional excitation/emission matrix (3DEEM) is the graph obtained by projecting the fluorescence intensity on the horizontal and vertical coordinates of the excitation wavelength and the emission wavelength. Its image is intuitive and contains rich information. It has the advantages of fast, high sensitivity, small sample size and no need for preprocessing and enrichment of samples, etc., and has been widely used in DOM composition and content analysis. According to the geological and hydrogeological conditions and aquifer distribution characteristics of Tahutu mine, the vertical distribution characteristics of groundwater chemistry in coal mine area were studied in this paper.

According to the classification method of natural organic matter in water, DOM three-dimensional fluorescence matrix of each aquifer in the study area mainly include (**Fig. 8**): I area (aromatic protein) - tyrosine, II area (aromatic protein and) - tryptophan, III area (like rich acid) - hydrophobic organic acids, IV area (dissolved microbial metabolites) - tryptophan-containing proteinlike, V area (like humic acid) -

Marine humic acid. Because DOM concentration in water is generally low, the type and intensity of DOM fluorescence peak are relatively weak.

In field surface water samples, there are 5 fluorescence peaks in DOM fluorescence matrix (**Fig. 13**): I area (aromatic protein) - tyrosine, fluorescence intensity (FI), FI=433.2QSU; II area (aromatic protein) - tryptophan, FI=433.4QSU; III area (like - fulvic acid) - hydrophobic organic acid, FI=551.9QSU; IV area (soluble microbial metabolites) - proteinoid containing tryptophan, FI=340QSU; V area (like - humic acid) - Marine humic acid, FI=555.7QSU. Surface water directly receives dissolved organic matter from surface flora and fauna and human activities, resulting in higher organic matter concentration and fluorescence intensity in water bodies.

Quaternary aquifer is mainly fed by overlay surface water and meteoric water, and DOM fluorescence spectrum matrix fingerprint in the water is mainly similar to that in surface water, showing two characteristics in 10 water samples. In the nine water samples collected from the surrounding civil mines, fluorescence peaks in I area, II area and V area (**Fig. 14**), and I area (aromatic protein) - tyrosine (FI = 384.6-560.8 QSU) were found, which is very significant and can be used as the symbol of Quaternary water of civil mines. The fluorescence peaks in the III area and V area are significantly different. In **Fig. 14 (a)**, the fluorescence peak intensities in I area and V area are 1334 QSU and 1378 QSU, respectively. In other water samples, the values are 70.52~509 QSU and 58.75~529 QSU respectively. In addition, DSG-1-2 is hydrological drilling water, and the fluorescence peaks in III area and V area mainly appear, FI =207.9 QSU and 202.6 QSU, indicating that I area (aromatic protein) substances are dissolved in the mine during application. In general, it can be seen from 3 DEEM finger pattern that the symbolic fluorescence peak in I area and the symbolic fluorescence peak between III area and V area appear in Quaternary water.

Because Zhidan Group is located in the lower part of Quaternary, groundwater recharge is relatively weak and water cycle time is longer, DOM fluorescence spectrum finger pattern in water samples is different from Quaternary water to some extent (**Fig. 15**), I area (aromatic protein) - tyrosine, FI=65.46~274.7QSU; II area (aromatic protein) - tryptophan, FI=76.27~306.8 QSU; V area (like - humic acid) - Marine humic acid, FI=100~376.7 QSU. In general, the concentration of dissolved organic matter in the groundwater of Cretaceous Zhidan Group is less than that of Quaternary, and the landmark fluorescence peak appears in V area (like - humic acid).

In the deeper Straight rom group aquifer, the groundwater has entered the deep retained circulation system, and although the DOM from shallow source is almost exhausted, there are three fluorescence peaks (**Fig. 16**), especially in ZLG-3-1 water sample, because the Zhiluo Formation belongs to a relatively water-rich aquifer, V area (like - humic acid) - Marine humic acid, FI=1701 QSU. This preliminary indicates that DOM from other sources exists in Straight rom group aquifer; three fluorescence peaks in the other three water samples, I area (aromatic protein) - tyrosine, FI=151.7~173.1 QSU; II area (aromatic protein) - tryptophan, FI=99.59~169.1QSU; V area (like - humic acid) - Marine humic acid, FI=150.3~622.5 QSU. Especially, the fluorescence peak intensity in V area is high, which further proves that DOM from other sources exists in the groundwater of Zhiluo Formation.

The aquifer of Yan'an group may be affected by roof inflow and geological deposition, and there are similarities and differences between the three - dimensional fluorescence spectra of the two groups. There are some differences within the Yan'an group, which can be divided into upper Yanan Formation and lower Yan'an group.

There are mainly three fluorescence peaks in the upper part of Yan'an group (Fig. 17), I area (aromatic protein) - tyrosine, FI=121.8~253.1 QSU; II area (aromatic protein) – tryptophan, FI=115.3~256.5QSU; V area (like - humic acid) - Marine humic acid, FI=157.9~611.1QSU. In addition, the fluorescence peak of III area in DCC-1-1-1 water sample, FI=894.6QSU. However, it does not appear in other water samples, which cannot be regarded as the organic hydrochemical characteristics of the upper aquifer of Yan'an group.

Three fluorescence peaks also appeared in the lower part of Yan'an group (Fig. 18), I area (aromatic protein) - tyrosine, FI=313.8~329.1 QSU; II area (aromatic protein) – tryptophan, FI=376.8 QSU; V area (like - humic acid) - Marine humic acid, FI=317.1~2613 QSU. In particular, the fluorescence peak in V area of the water sample in **Fig. 18 (a)**, FI=2613 QSU. It is suggested to continue to collect water samples from the lower part of Yan'an group in the later underground mining process to further determine the organic hydrochemical characteristics of the lower part of Yan'an group.

In general, each aquifer in the Taohutu mine field can be divided into several characteristics: Fluorescence peaks in I area and III area mainly appear in surface water and Quaternary water, and DOM sources in surface water are more abundant; fluorescence peak in I area also appears in the water of Zhidan Group, Straight Rom Group and Yan'an Group, and the fluorescence peak between I area and II area is a symbol. In addition, the fluorescence peak in V area is also a symbol; Cretaceous → Straight Rom Group → Yan'an Group. The fluorescence peak intensity in V area showed an increasing trend, indicating the existence of humus-like DOM from other sources in the deep aquifer.

Conclusion

Through the comprehensive detection and analysis of inorganic hydrochemical characteristics, isotopes and organic hydrochemical characteristics of the water samples in Taohutu mine field, combined with the hydrogeological data of the mine, the hydrochemical characteristics of the aquifer in Taohutu mine field can be obtained. By distinguishing the differences in hydrochemical characteristics of each aquifer, the conclusions are drawn as follows:

Mineralization of shallow aquifers (surface water bodies, Quaternary and Luohe Formation) < 500mg/L, the cation is mainly Ca^{2+} , the anion is mainly HCO_3^- , which belongs to $\text{HCO}_3\text{-Ca}\cdot\text{Mg}$ type water. It shows that the shallow aquifer (body) receives the replenishment of meteoric water, the runoff condition is relatively good, and the cycle alternates positively. The water salinity of deep aquifers (Straight Rom Group, Yan 'an Group) is general > 3500mg/L, the cation is mainly Na^+ , the anion is mainly SO_4^{2-} , it belongs to $\text{SO}_4\text{-Na}$ water, that is, high salinity, Na^+ and SO_4^{2-} ions dissolved in large quantities, showing obvious hydrochemical characteristics different from the shallow aquifer.

According to the analysis of hydrochemical characteristics, there is no direct hydraulic connection between Luohe Formation and Straight Rom Group. Combined with the hydrogeological data and groundwater runoff of Tahutu mine field, it is found that the change rule of the total hydrochemical types from shallow aquifer to deep aquifer in Tahutu mine field is as follows: $\text{HCO}_3\text{-Ca}\cdot\text{Mg}\rightarrow\text{HCO}_3\text{-Na}\rightarrow\text{SO}_4\text{-Na}$.

The results of environmental isotopes (D and ^{18}O) indicate that the rainwater, surface water and Quaternary water belong to modern groundwater, while Zhidan Group water is between the modern groundwater and the ancient water; in the deep Straight Rom Group and Yan'an Group, the values of δD and $\delta^{18}\text{O}$ are low, and the groundwater falls below the rainwater line of Ordos Basin with a deep circulation depth. Before mining, the groundwater is in the stagnant state with good closed conditions.

The content of dissolved organic matter (TOC and UV_{254}) in groundwater decreases gradually with the increase of aquifer depth; fluorescence peaks in I area and the II area mainly appeared in surface water and Quaternary water, and DOM sources in surface water were more abundant; fluorescence peak in I area also appears in the water of Zhidan Group, Straight Rom Group and Yan'an Group, and the fluorescence peak between I area and II area is a symbol. In addition, the fluorescence peak in V area is also a symbol; Cretaceous \rightarrow Straight Rom Group. The fluorescence peak intensity in V area showed an increasing trend, indicating the existence of humus-like DOM from other sources in the deep Straight Rom Group aquifer.

By analyzing the water chemical characteristics of aquifer in Tahutu mine field, this paper establishes the background data of water chemistry of different aquifer in this mine field, so as to quickly judge the source of water inrush when the mine encounters unknown water inrush or water disaster accident in the future, and provide scientific basis and technical guidance for the accurate and rapid response to water disaster and the formulation of reasonable water control measures.

Declarations

Data Availability

Some or all data, models, or code generated or used during the study are available from the corresponding author by request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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Figures

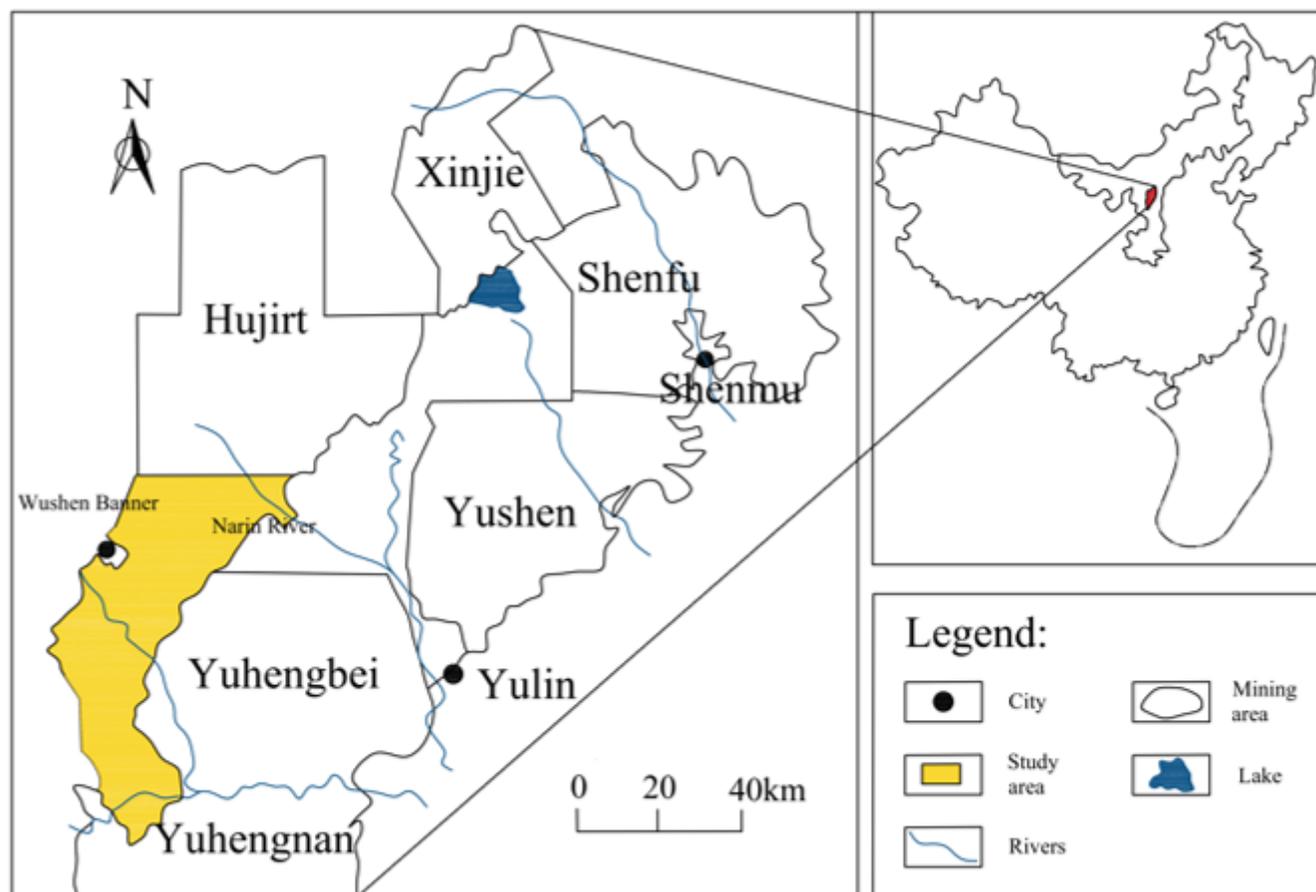


Figure 1

Location Diagram of the study area Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

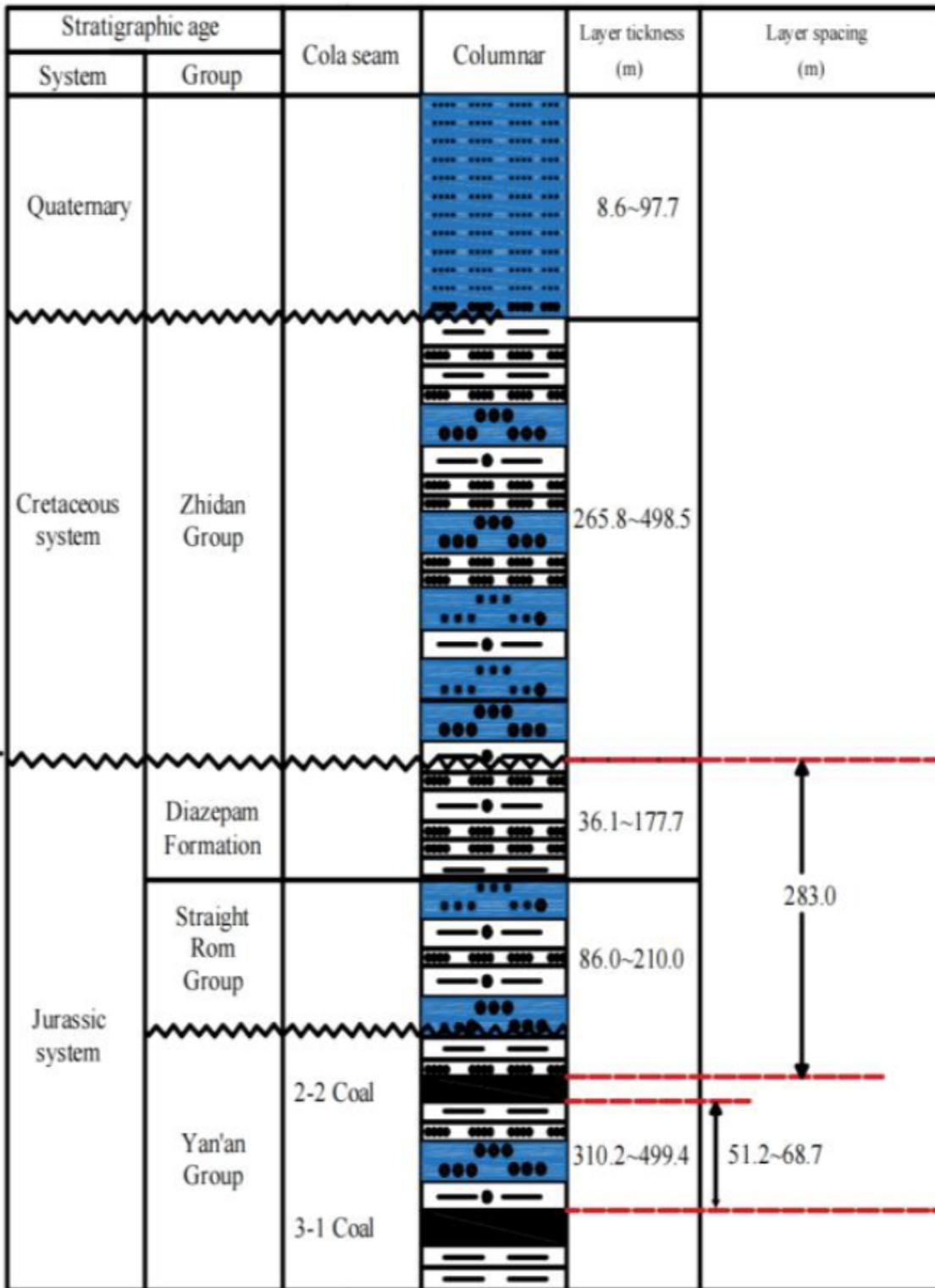


Figure 2

Hydrogeology histogram of the study area

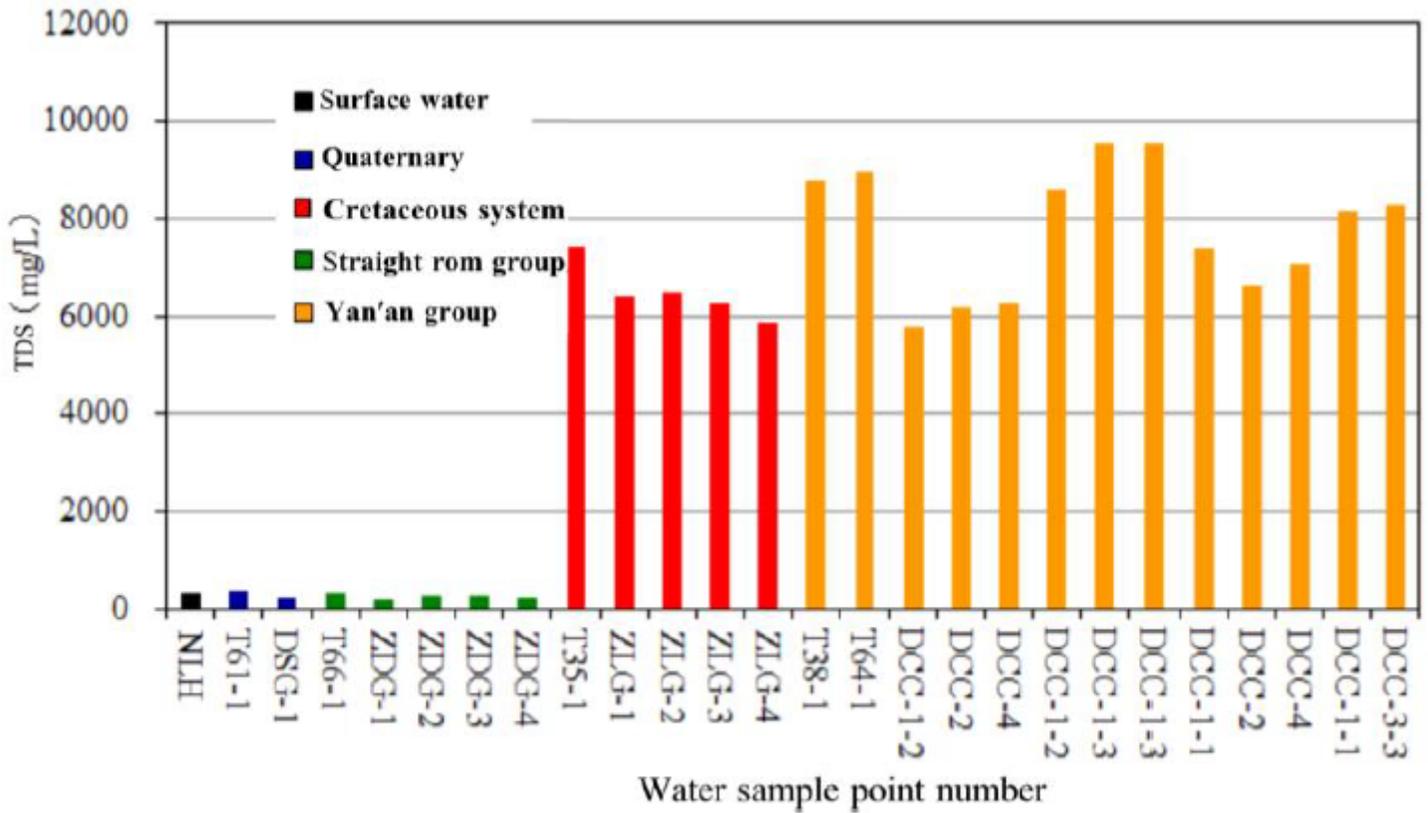


Figure 3

TDS concentration in each aquifer in the study area

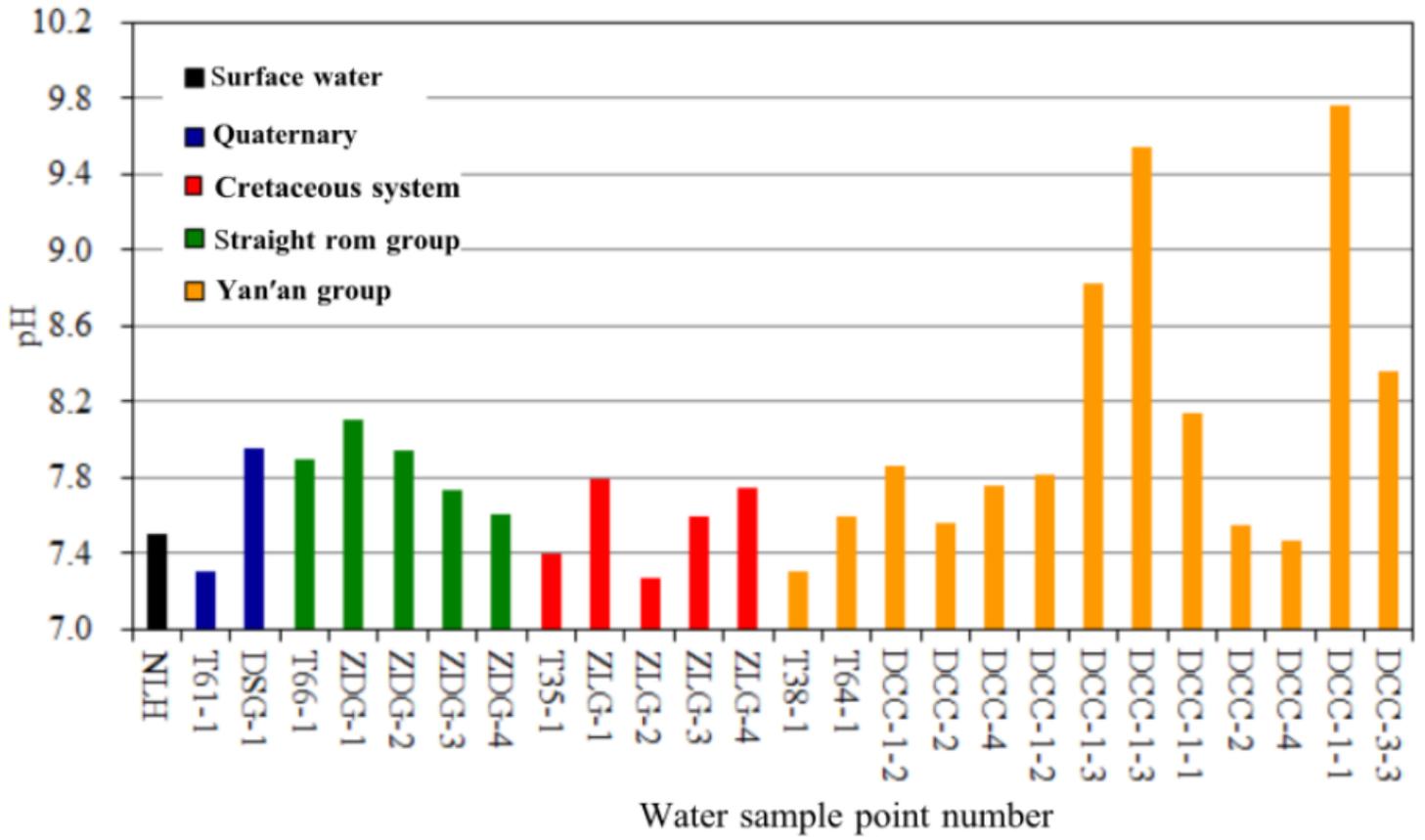


Figure 4

pH values of each aquifer in the study area

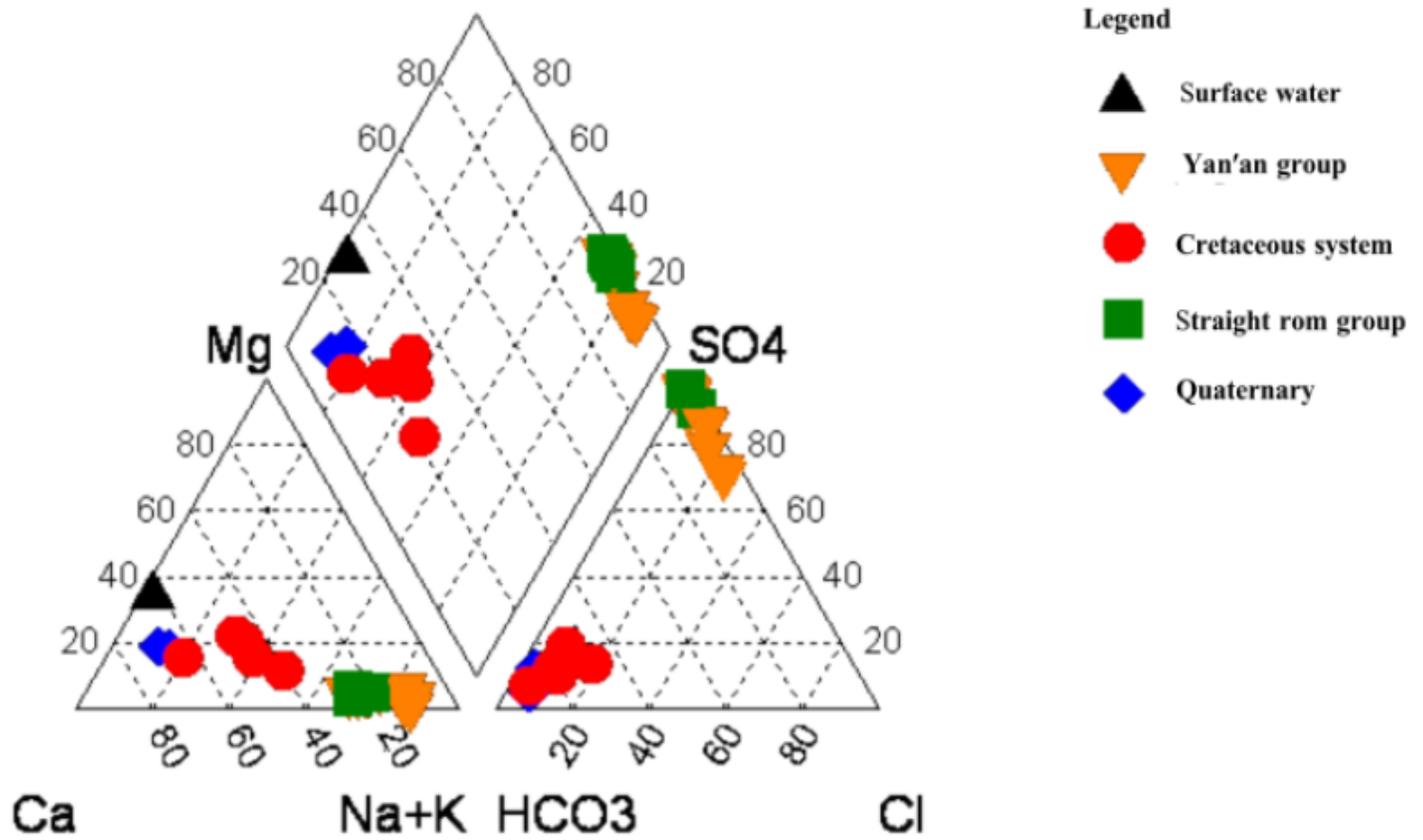


Figure 5

Hydrochemical piper trilinear diagram of each aquifer

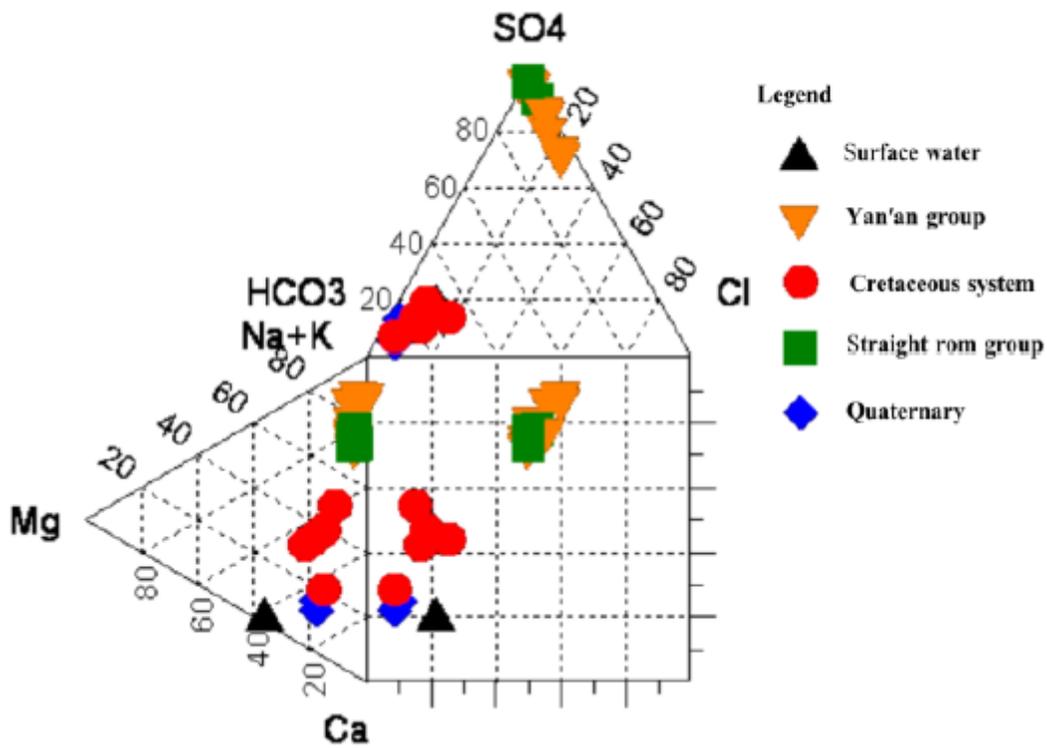


Figure 6

Durov chart of hydrochemistry of each aquifer

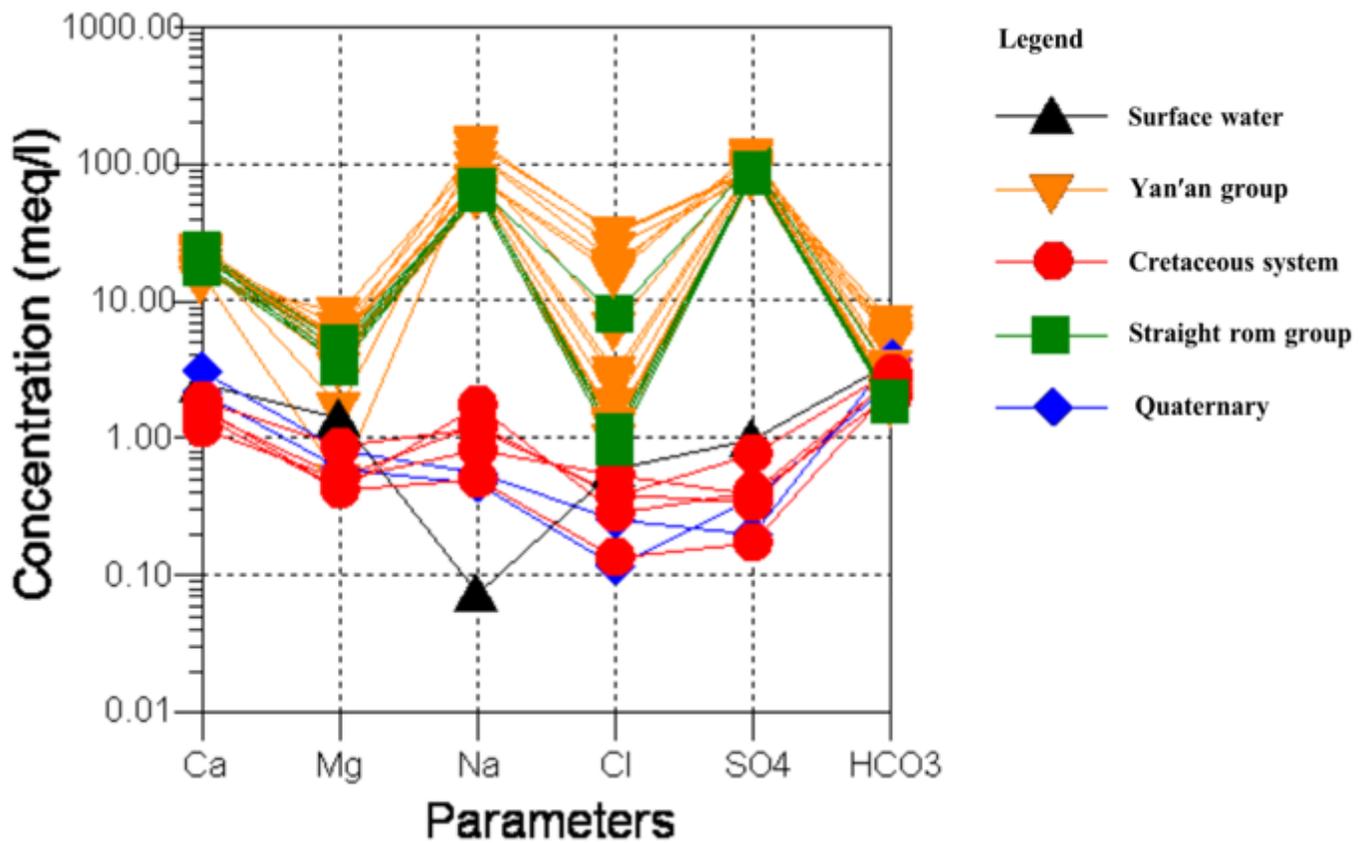
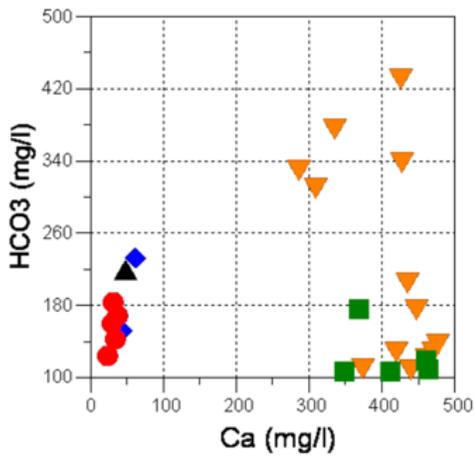
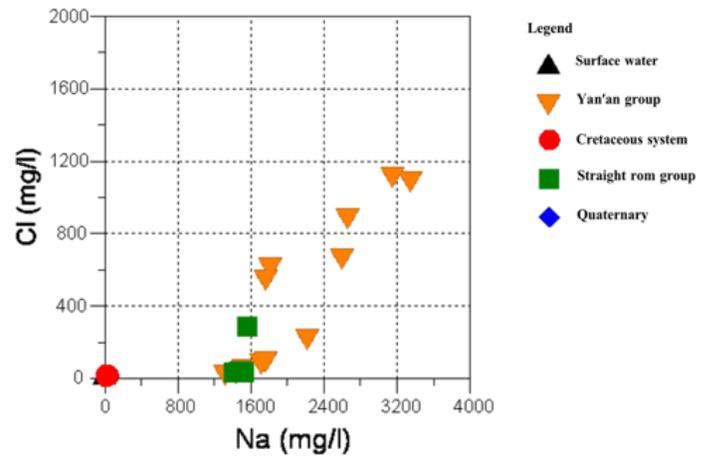


Figure 7

Schoeller chart of the hydrochemistry of each aquifer



(a) HCO₃⁻, Ca²⁺ ions Scatter



(b) Cl⁻, Na⁺ ions Scatter

Figure 8

Scatter chart of the hydrochemistry of each aquifer

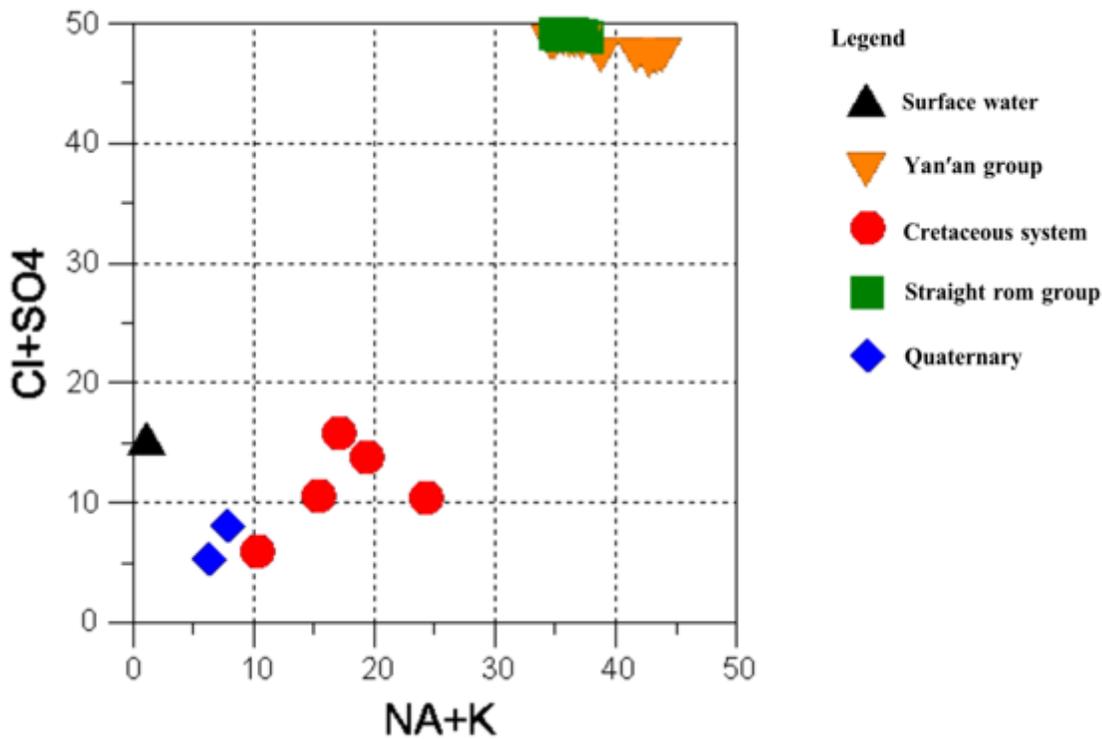


Figure 9

Ludwig Langelier chart of the hydrochemistry of each aquifer

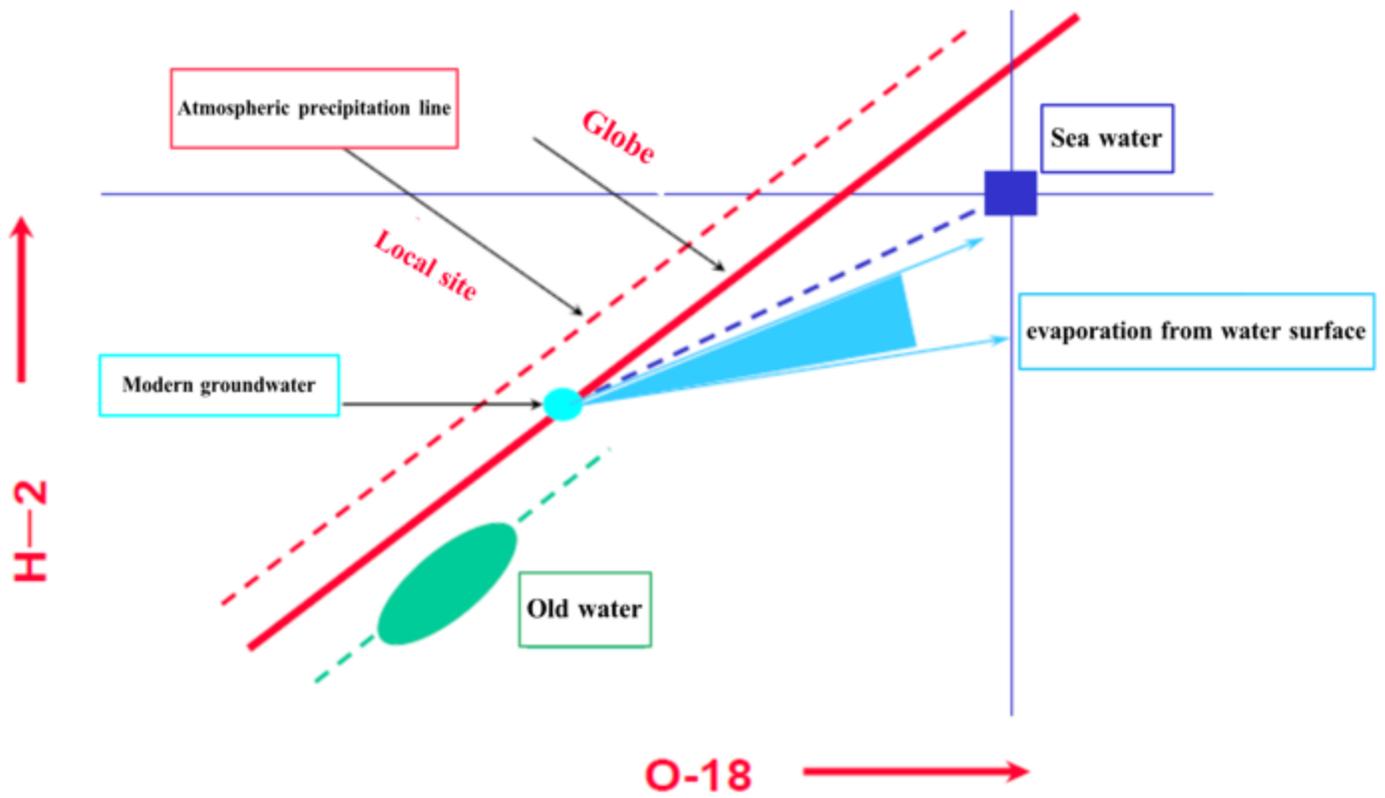


Figure 10

Diagram of δD vs $\delta^{18}O$ relationship of different water sources

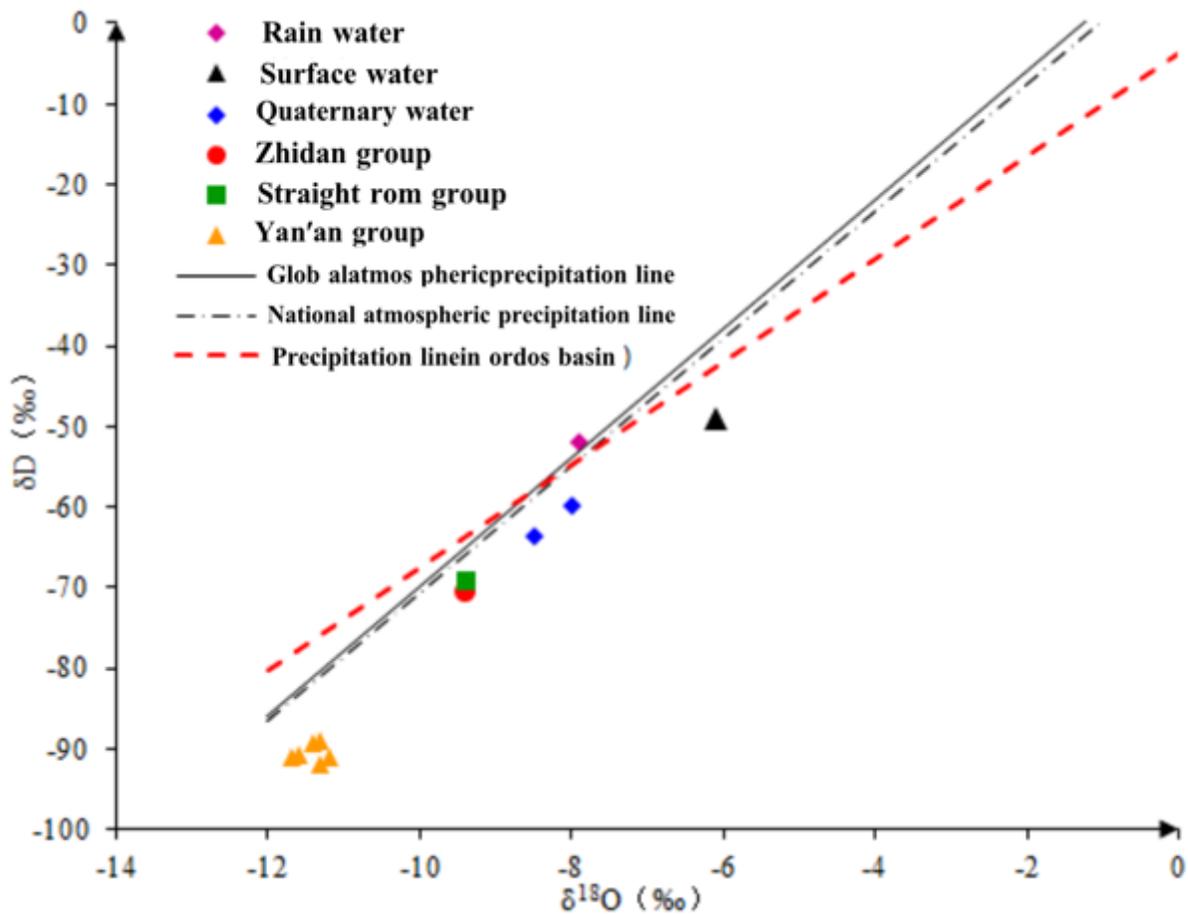


Figure 11

Diagram of δD vs $\delta^{18}O$ relationship of different water sources

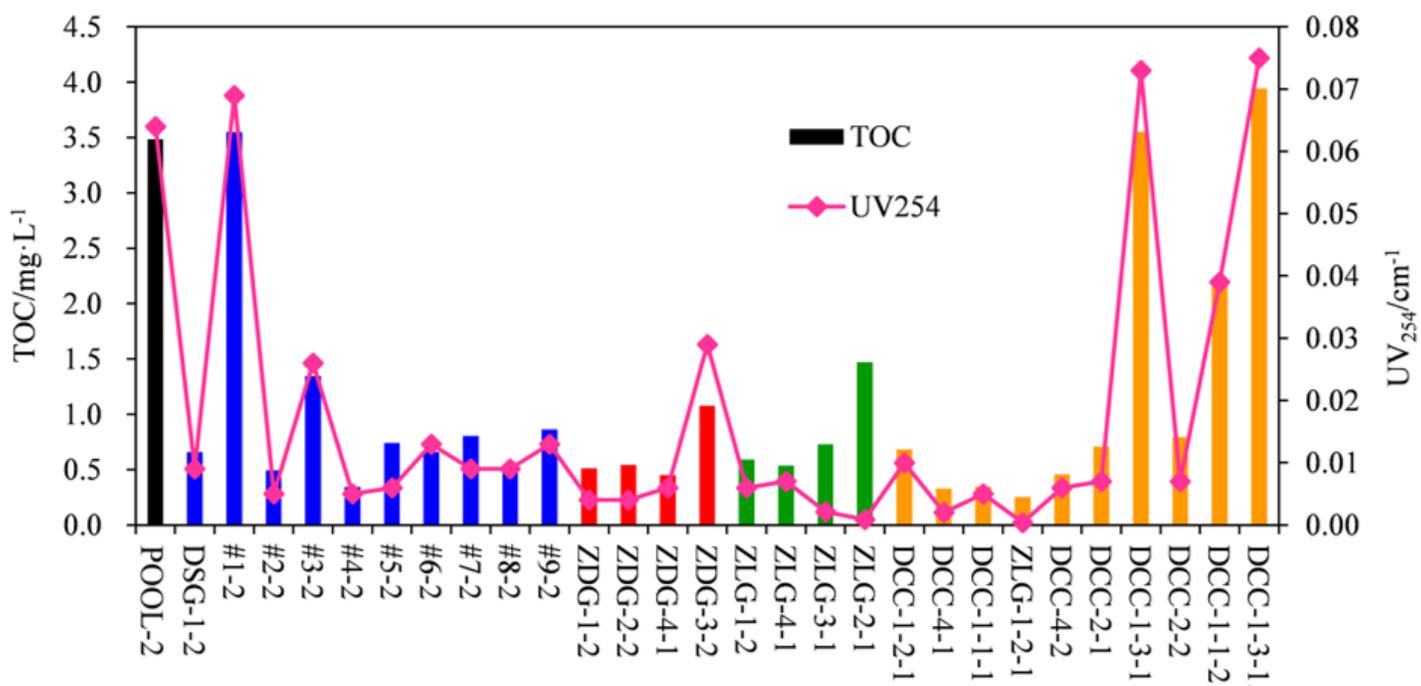


Figure 12

Characteristics of TOC and UV254 concentrations in groundwater

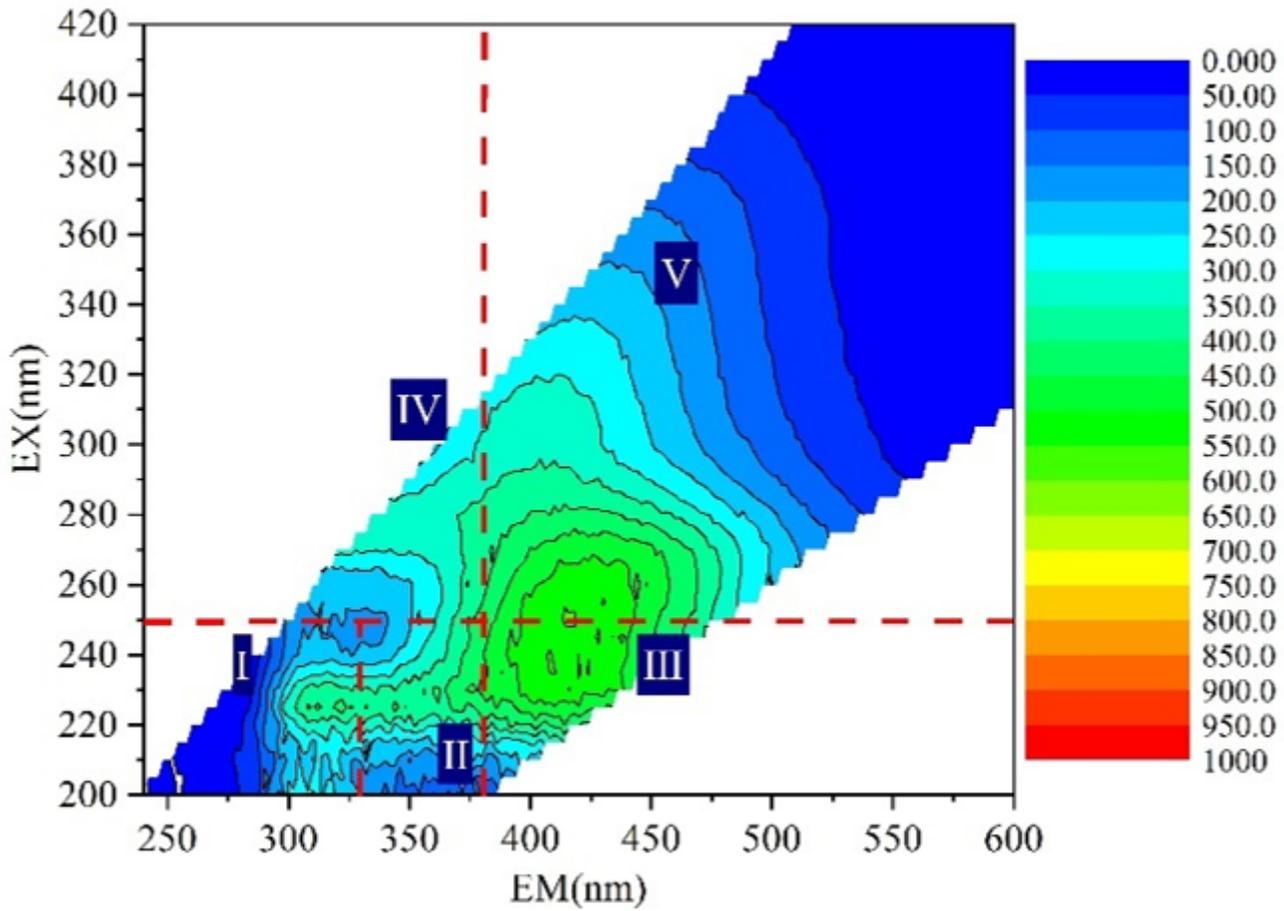


Figure 13

DOM fluorescence matrix of surface water (pool -2)

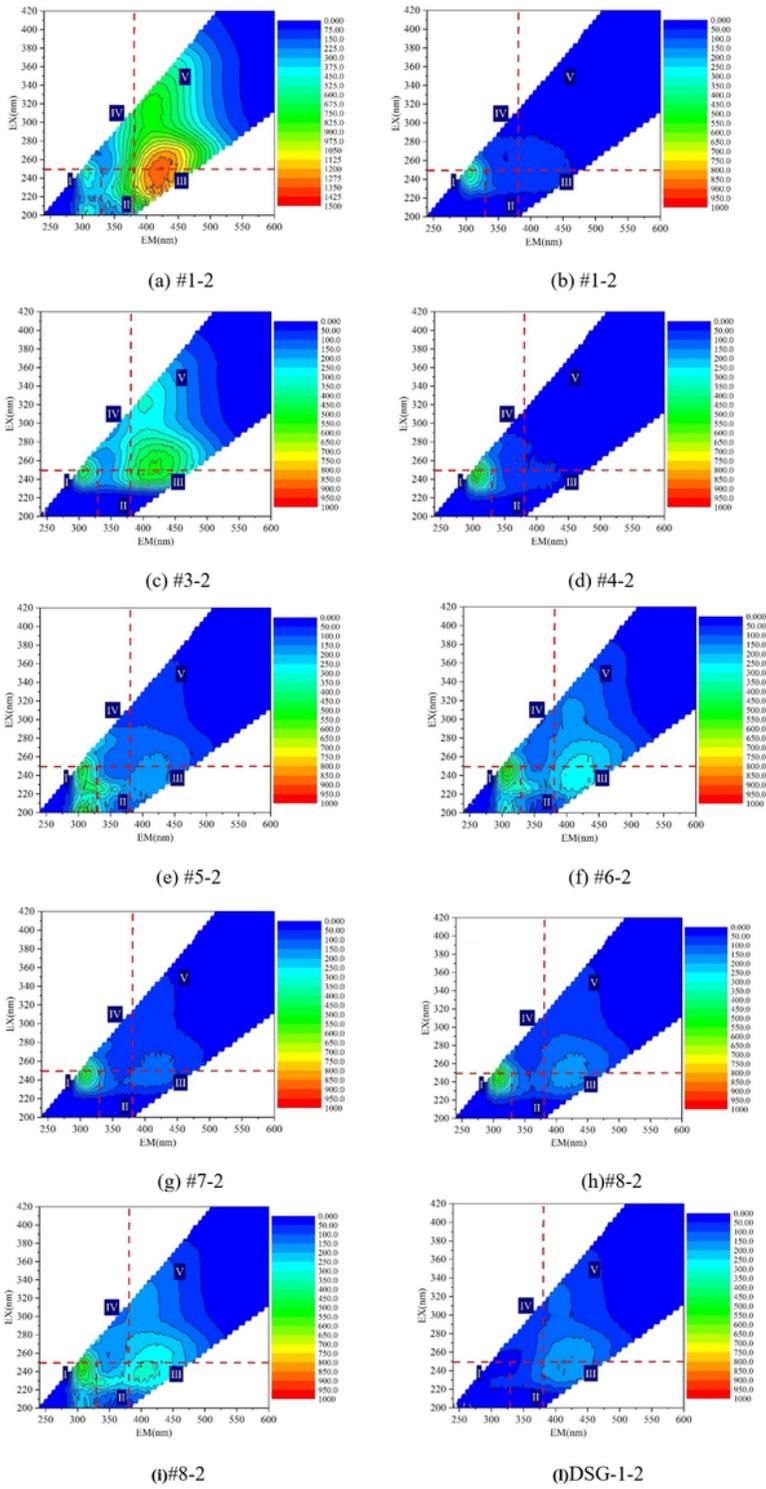
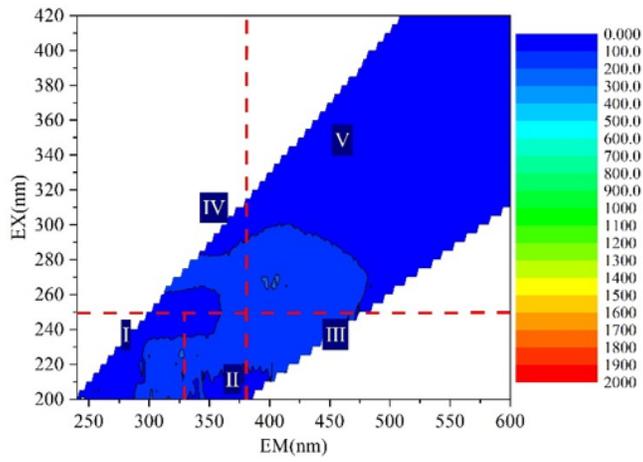
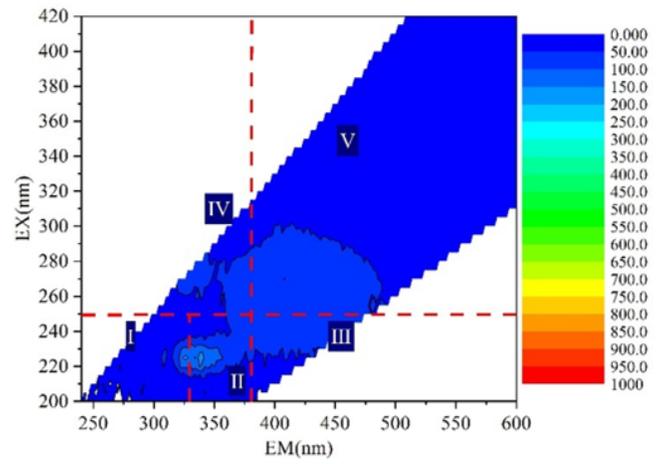


Figure 14

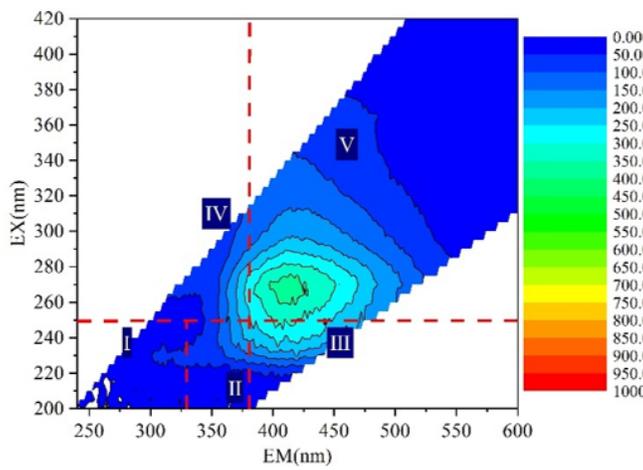
DOM fluorescence matrix of Quaternary water samples



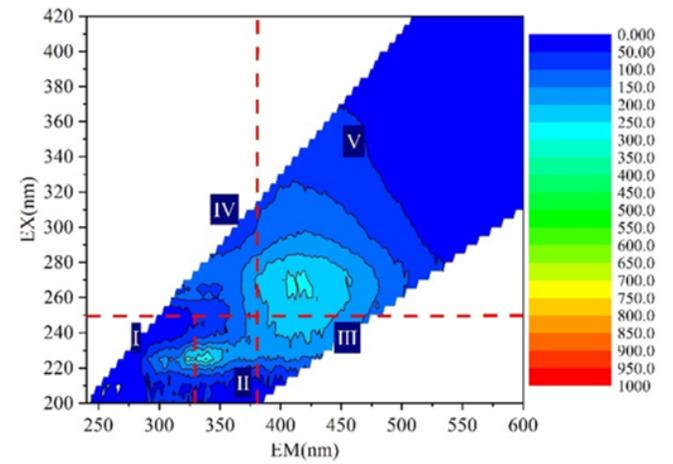
(a) ZDG-1-2



(b) ZDG-2-2



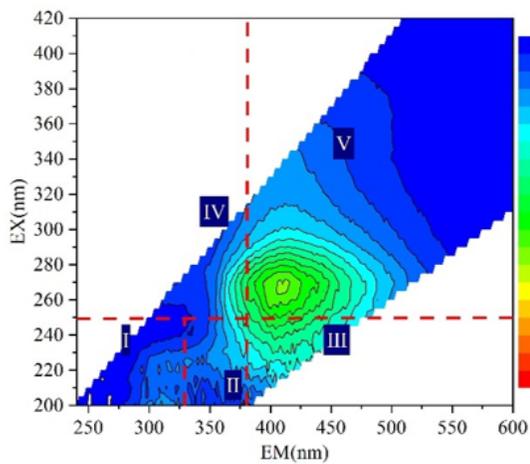
(c) ZDG-3-2



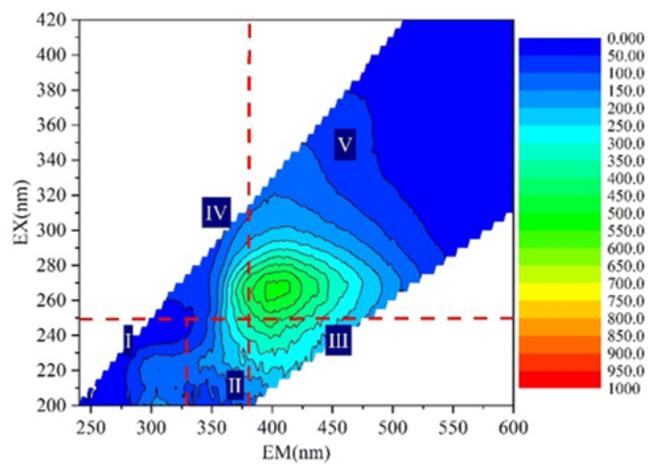
(d) ZDG-4-1

Figure 15

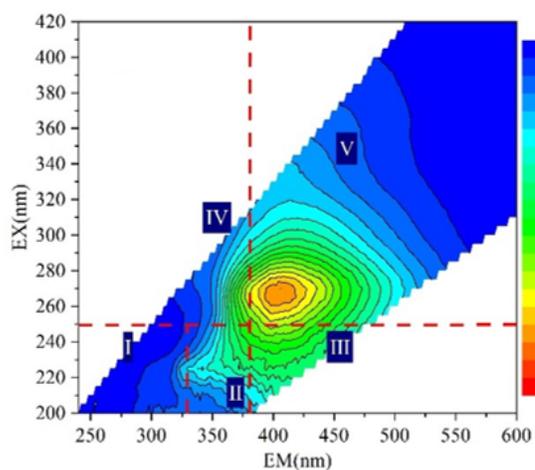
DOM fluorescence matrix of Zhidan Group water samples



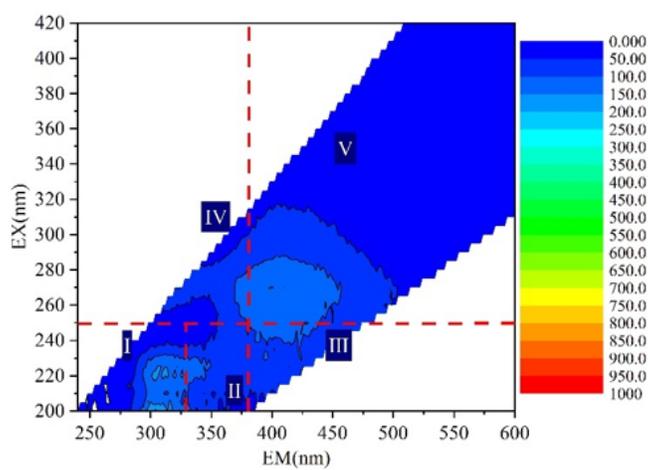
(a) ZLG-1-2



(b) ZLG-2-1



(c) ZLG-3-1



(d) ZLG-4-1

Figure 16

DOM fluorescence matrix of Straight rom group water samples

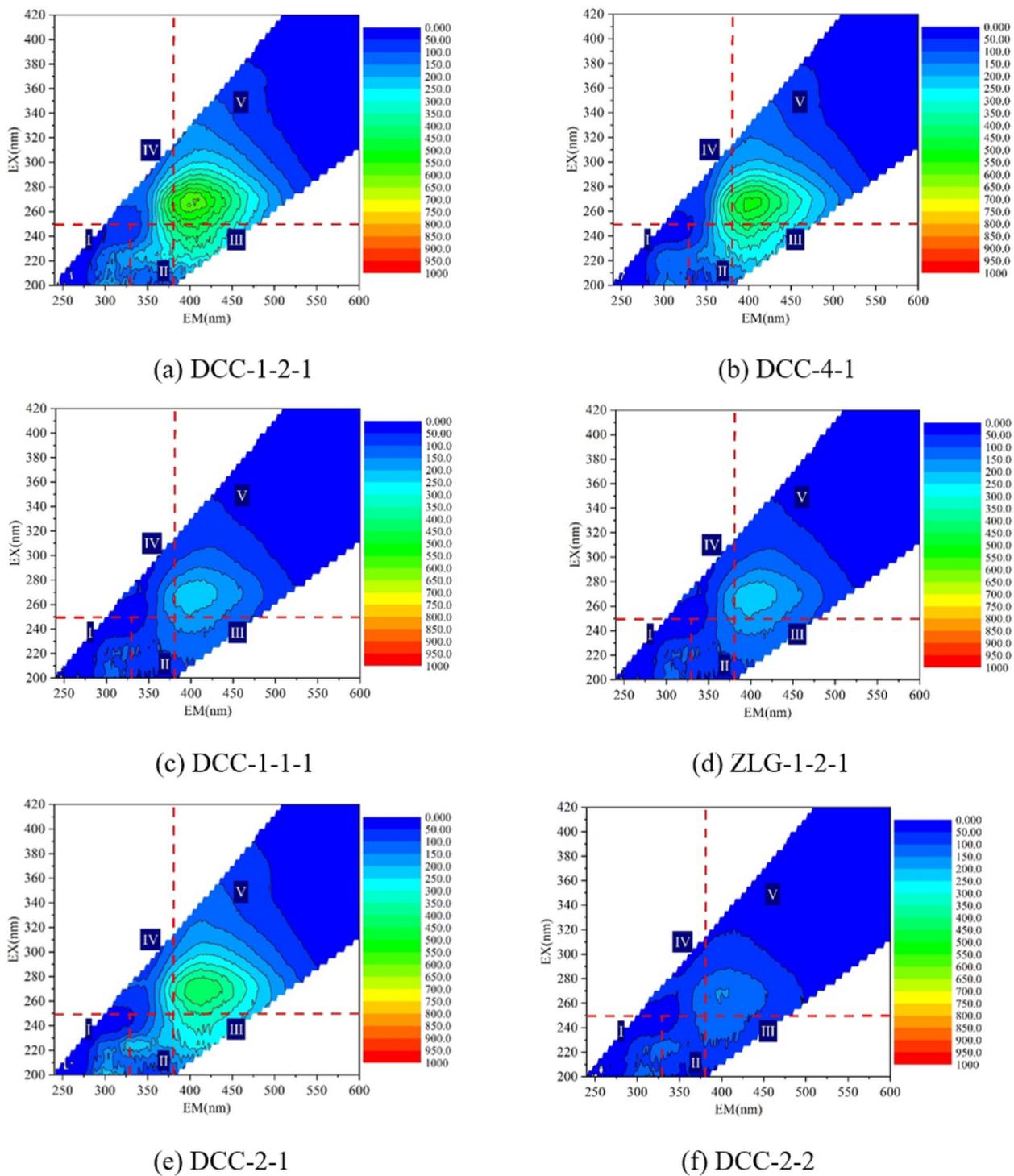
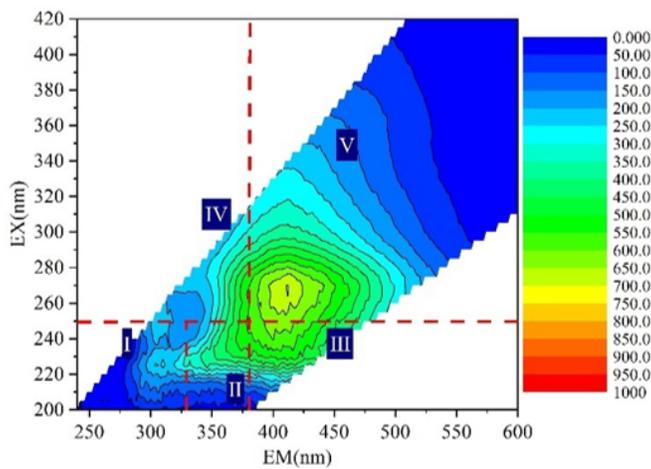
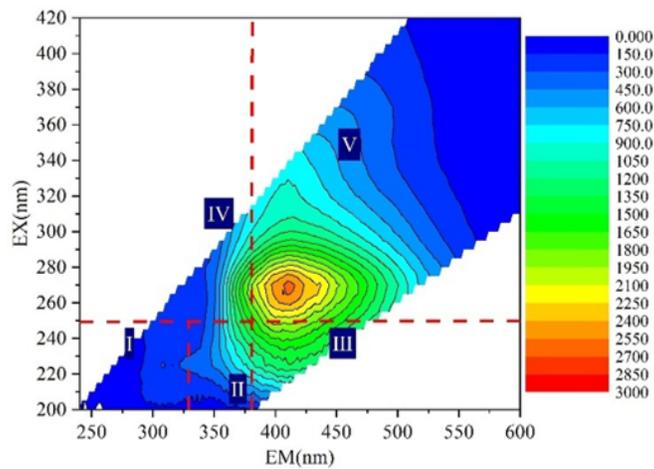


Figure 17

DOM fluorescence matrix of upper water samples of Yan'an group



(a) DCC-1-1-2



(b) DCC-1-3-1

Figure 18

DOM fluorescence matrix of water samples in the lower Yan'an group