ABSTRACT: Iron and manganese ions, as the main contribution indicator of super-class III shallow groundwater in the western suburbs of Xi'an, seriously threaten the safety of local water supply and the health of residents. Based on data collection and hydrogeological survey, this paper studies the concentration of iron and manganese in groundwater by collecting and analyzing 52 groups of groundwater samples, and analyzes the possible sources of iron and manganese in consideration of human factors such as hydrogeological conditions and surface pollution input. The results showed: (1) The highest iron content exceeded the Class III water quality standard by 1.03 times, and the highest manganese content exceeded the Class III water quality standard by 3.92 times. The water sample points exceeding Class III accounted for 9.5% and 26.2% of the total water sample points respectively. (2) The content of iron and manganese in the water of Feng River is 8.47% and 19.69% of the groundwater respectively. Therefore, the higher iron and manganese in individual wells near the source of Feng River have no obvious relationship with Feng River. (3) According to drilling data, the iron and manganese content in different rock masses is silty clay>round gravel>fine sand, medium-coarse sand, and the distribution of iron and manganese content is positively correlated. (4) In the experiment of the iron and manganese release law in the rock mass, it was observed that the iron and manganese in the overlying water experienced three stages of rapid increase, fall and stabilization. When the final release stabilizes, the release rate of manganese in the rock mass is higher than that of iron. The manganese content in the overlying water is 0.010~0.057mg/L, the release rate is 0.02%~0.05%, and the iron content is 0.004~0.023mg/ L, the release rate is less than 0.01%, and the higher pH in the water environment has a significantly higher inhibitory effect on the release of iron in the rock mass than manganese.

Keywords: Hydrogeochemistry; water pollution; Fe ion; Mn ion

1. INTRODUCTION

Water resources play an important role in promoting orderly economic development, ensuring the basic lives of urban and rural residents, and maintaining ecological balance. Surface water and groundwater are important components of water resources. Compared with surface water, groundwater is more widely distributed and requires less investment in mining and utilization. Especially in some arid and semi-arid areas, surface water resources are relatively scarce, and the role of groundwater is particularly obvious. In the development and utilization of groundwater, the riverside groundwater source has sufficient water quantity and good water quality, so riverside mining has become an important method of groundwater utilization.

In recent years, due to the intensification of human activities, the impact on groundwater is increasing and the dependence is increasing. While developing and utilizing groundwater resources, we are facing one of the most serious problems-groundwater pollution. Groundwater pollution refers to the phenomenon that groundwater quality is deteriorating under the influence of human activities. In addition to the impact of human activities, the natural geological environment may also have inferior quality water[1-5]. In the evaluation of groundwater pollution, it is difficult to determine the background value or the control value due to the influence of human activities. It often includes groundwater pollution caused by some natural factors, which exaggerates the evaluation results and cannot correctly provide a scientific basis for proposing groundwater pollution prevention measures[6-11]. According to data, the quality of most of the shallow groundwater in Xi'an is mainly Fe, Mn, and ammonia nitrogen. Among them, Fe and Mn are listed as secondary pollutants in the "Secondary Drinking Water Standards: Guidance for Nuisance Chemicals" issued by the US Environmental Protection

Agency[12]. Therefore, the analysis of pollutants in the water source area can not only grasp the pollution status of groundwater, but also predict the size of its pollution risk, so as to provide a more scientific basis for pollution prevention and groundwater resources exploitation planning. In addition, scholars from Spain, Turkey, etc. are also conducting continuous research on the distinction between man-made and natural factors on groundwater[13-17].

2. Research area situation

2.1 General situation of physical geography of Feng River Basin

2.1.1 Geographical location of the study area

Located in the northwest of Xi'an, Shaanxi Province, Feng River is a primary tributary of the Wei River, a tributary of the Yellow River. It is located at 108°35′~109°09′ east longitude and 33°50′~34°20′ north latitude. It has a total length of 78km and a drainage area of 1380km². The annual average runoff is 423 million m³. It flows through Chang'an District, Hu County, Fengdong New City and Qindu District of Xianyang City. The study area is located in the lower reaches of Feng River (Figure 1).

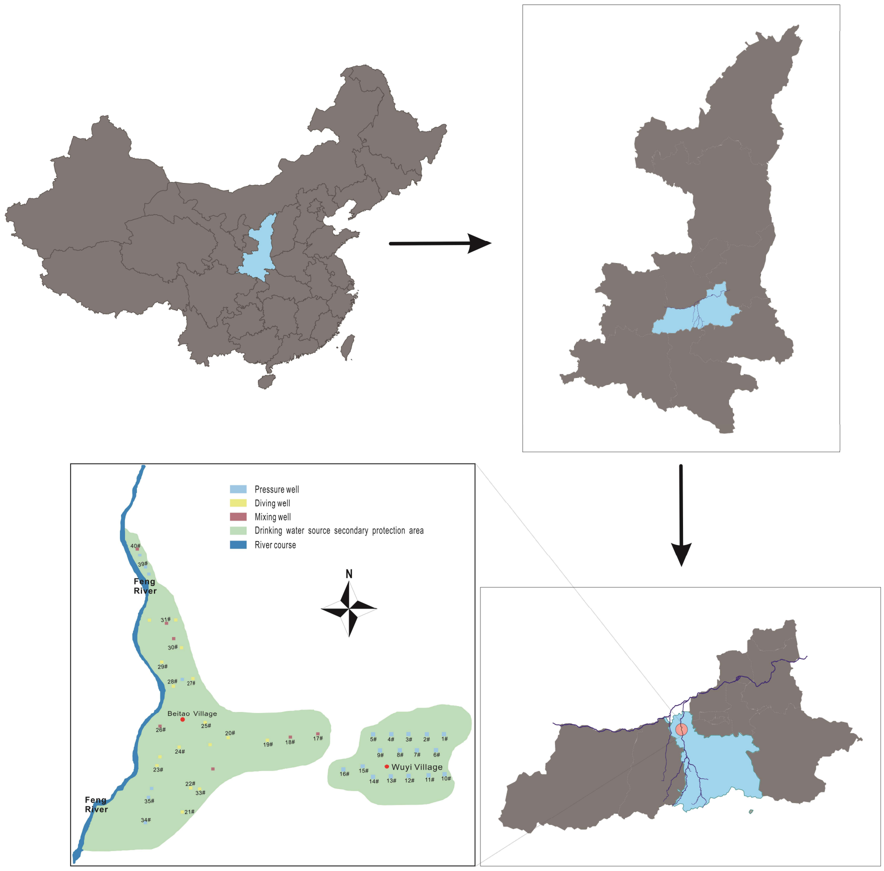


Figure 1. Geographical location of the research area

2.1.2 Topography

The Feng River flows from south to north, borders the Qinling Mountains in the south, and flows into the Wei River in the north. Generally speaking, it is high in the southeast and low in the northwest (Figure 2). The upper reaches of the river valley is relatively wide, the slope is relatively gentle, the river bed is mainly pebbles, the soil on both sides of the river is thin, the river water seepage ability is strong, and the infiltration situation is serious. The lower reaches of the river are relatively straight, the flow rate of the river is slow, a large amount of sediment in the river is deposited, the river bed is higher, and the two banks of the river form a vast alluvial plain.

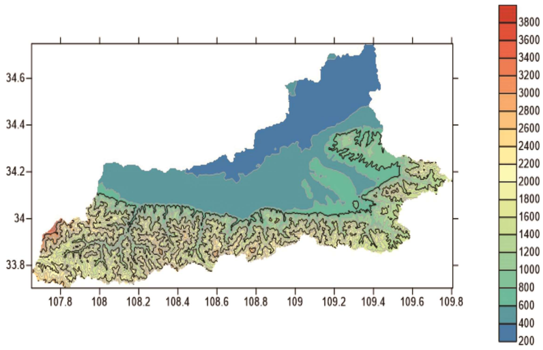


Figure 2. Xi'an City Elevation

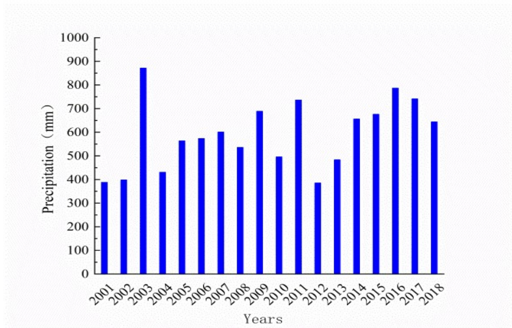


Figure 3. Histogram of annual precipitation distribution in Xi'an from 2001 to 2018

2.1.3 Formation lithology

The landform types around the study area are mainly floodplains, first-level terraces and second-level terraces formed by the erosion and accumulation of Wei, Feng and Zao rivers. The area is widely covered by the Fourth System. The drill hole is located in the middle of the Feng first terrace. Coordinates east longitude: 108° 45′20.8″ north latitude 34°17′10.2″ and the borehole depth is 285m. The borehole revealed: Lower alluvial deposits of the Holocene series (Q_4^{1al}), Middle Pleistocene alluvial horizon (Q_2^{al}) and Alluvial lacustrine strata of Lower Pleistocene (Q_1^{al+l}) (Table 1).

2.1.4 Hydrometeorology

The Feng River Basin has a warm temperate semi-humid continental monsoon climate with four seasons, cold and warm, dry and wet. The annual average temperature is 13.3℃, the coldest January average temperature is -1.3℃~0.5℃, and the hottest July average temperature is 26.3℃~26.6℃.

According to data from Xi'an Meteorological Bureau(Figure 3)， the average annual precipitation is 522.4~719.5mm, and it is mainly concentrated in July to September, accounting for 45% to 60% of the annual precipitation. The geographic distribution of precipitation is affected by topography. The overall precipitation trend gradually increases from north to south, with obvious differences; from east to west, there is also an increasing trend, but the trend is not very obvious. The annual sunshine hours are 1646.1~2114.9 hours. The regional distribution of evaporation is opposite to precipitation. It gradually decreases from north to south. The distribution is uneven during the year. Winter temperature is low and evaporation is low. From November to January of the following three months Evaporation only accounts for 9.6% of the annual evaporation. In summer, the temperature is high and the evaporation is relatively large. The three-month evaporation from June to August accounts for about 43.4% of the annual evaporation.

Table 1. Formation lithology distribution statistics table

Quaternary System	Numbering	Depth (m)	Rock thickness (m)	Lithology
Lower alluvial deposits of the Holocene series (Q_4^{1al})	1	0~1.7	1.7	plain fill
	2	1.7~3.0	1.3	loess
	3	3.0~7.8	4.8	Fine sand
	4	7.8~15.0	7.2	Coarse sand
	5	15.0~19.9	4.9	Round gravel
Middle Pleistocene	6	19.9~26.5	6.6	Fine sand

alluvial horizon (Q_2^{al})	7	26.5~29.8	3.3	Coarse sand
	8	29.8~36.1	6.3	Fine sand
	9	36.1~40.0	3.9	Round gravel
	10	40.0~41.3	1.3	Silty clay
	11	41.3~52.0	10.7	Fine sand
	12	52.0~65.0	13.0	Coarse sand
	13	65.0~67.0	2.0	Fine sand
	14	67.0~67.5	0.5	Silty clay
	15	67.5~70.0	2.5	Coarse sand
	16	70.0~74.8	4.8	Round gravel
	17	74.8~78.2	3.4	Silty clay
	18	78.2~80.0	1.8	Fine sand
	19	80.0~92.9	12.9	Coarse sand
	20	92.9~96.4	3.5	Silty clay
	21	96.4~142.0	45.6	Coarse sand
	22	142.0~145.0	3.0	Silty clay
	23	145.0~147.8	2.8	Coarse sand
	24	147.8~154.8	7.0	Round gravel
	25	154.8~179.5	24.7	Coarse sand
	26	179.5~184.0	4.5	Fine sand
	27	184.0~187.5	3.5	Coarse sand
	28	187.5~191.0	3.5	Round gravel
	29	191.0~250.5	59.5	Coarse sand
Alluvial lacustrine strata of Lower Pleistocene (Q_1^{al+l})	30	250.5~256.0	6.0	Silty clay
	31	256.0~261.0	5.0	Fine sand
	32	261.0~268.0	7.0	Round gravel
	33	268.0~285.0	17	Coarse sand

2.2 Current status of water resources development and utilization

The underground water source of the Feng River is located on the east bank of the Feng River floodplain and the rear edge of the first terrace, and is located in the front edge of the alluvial plain. It was put into production in 1961 and is a riverside water source. The aquifer in the groundwater source area has small buried depth and good water permeability. The mining is mainly based on diving with a buried depth of more than 80m. The replenishment is mainly based on natural precipitation, river water lateral seepage and irrigation back seepage. Therefore, this article mainly focuses on the diving in the water source area. Object. According to the survey, there are 26 wells designed for this groundwater source. Up to now, there are 21 water wells, of which 16 wells are used for diving, accounting for 76.2% of the existing water wells. The average water head depth is 28m, which has been stable in recent years. In the mining state, the current water supply capacity is 20,000 m^3 /d.

3. SAMPLE COLLECTION AND TESTING

3.1 Sample collection

Taking mixed water samples from 13 pumping single wells in the water source protection area and the third water supply plant in Xi'an as the survey objects, 14 groups of groundwater samples were collected in May, June and July 2019, a total of 52 groups, sampling points Covers all areas of the water source. The specific sampling locations and latitude and longitude coordinates are shown in the table 2 and Figure 4.

Table 2. Geographical location and time of sampling point

Well number	Sampling date the first time	the second time	the third time	Longitude(E)	Latitude(N)
17#	2019.05	2019.06	2019.07	108°47′05.88″	34°16′48.86″
18#	2019.05	2019.06	2019.07	108°46′48.50″	34°16′48.83″
19#	2019.05	2019.06	2019.07	108°46′14.50″	34°16′48.84″
23-1#	2019.05	2019.06	2019.07	108°44′51.22″	34°16′49.87″
23-2#	2019.05	2019.06	2019.07	108°44′51.44″	34°16′49.96″
26-2#	2019.05	2019.06	2019.07	108°45′06.15″	34°17′19.64″
27-1#	2019.05	2019.06	2019.07	108°45′09.36″	34°17′39.24″
27-2#	2019.05	2019.06	2019.07	108°45′08.80″	34°17′39.11″
28#	2019.05	2019.06	2019.07	108°44′54.04″	34°17′36.37″
30-1#	2019.05	2019.06	2019.07	108°44′59.40″	34°18′07.31″
31-1#	2019.05	2019.06	2019.07	108°44′55.39″	34°18′27.26″
31-2#	2019.05	2019.06	2019.07	108°44′55.31″	34°18′27.56″
40#	2019.05	2019.06	2019.07	108°44′45.79″	34°19′1.57″
Mixed	2019.05	2019.06	2019.07	108°48′27.86″	34°16′39.55″

Before collecting water samples turn on the pump and let it work for 15 minutes before collecting fresh water samples to ensure that the collected groundwater samples are representative. Before sampling, rinse with deionized water 3 times, and then rinse 3 times with the water sample to be collected. Make sure that the collected water sample fills the sampling bottle when sampling. Two bottles of water samples are collected at the same sampling point. The container used for sampling is a 2.5L polyethylene barrel, which is not processed for anion analysis. 1L polyethylene bottle is acidified with nitric acid (superior grade) to pH ＜2 for cationic analysis , Measure the pH and oxidation-reduction potential (Eh) of the water sample on site, store the sample at low temperature after labeling, and send it to the laboratory for testing within 2 hours[18](Table 3).

Table 3. pH and oxidation-reduction potential (Eh)

Project	Month	Max	Minimum	The average value	Median	Coefficient of Variation
pH	May	8.46	7.71	8.17	8.21	2.55
	June	8.3	7.89	8.18	8.22	1.57
	July	8.32	7.94	8.16	8.17	1.19
Eh（mV）	May	-16.4	-123.8	-73.9	-70.3	1.04
	June	-16.3	-122.7	-66.2	-69.9	1.14
	July	-16.8	-123.2	-68.4	-69.1	1.10

3.2 Testing method

Testing methods and testing instruments used in the process of groundwater quality testing (Table 4):

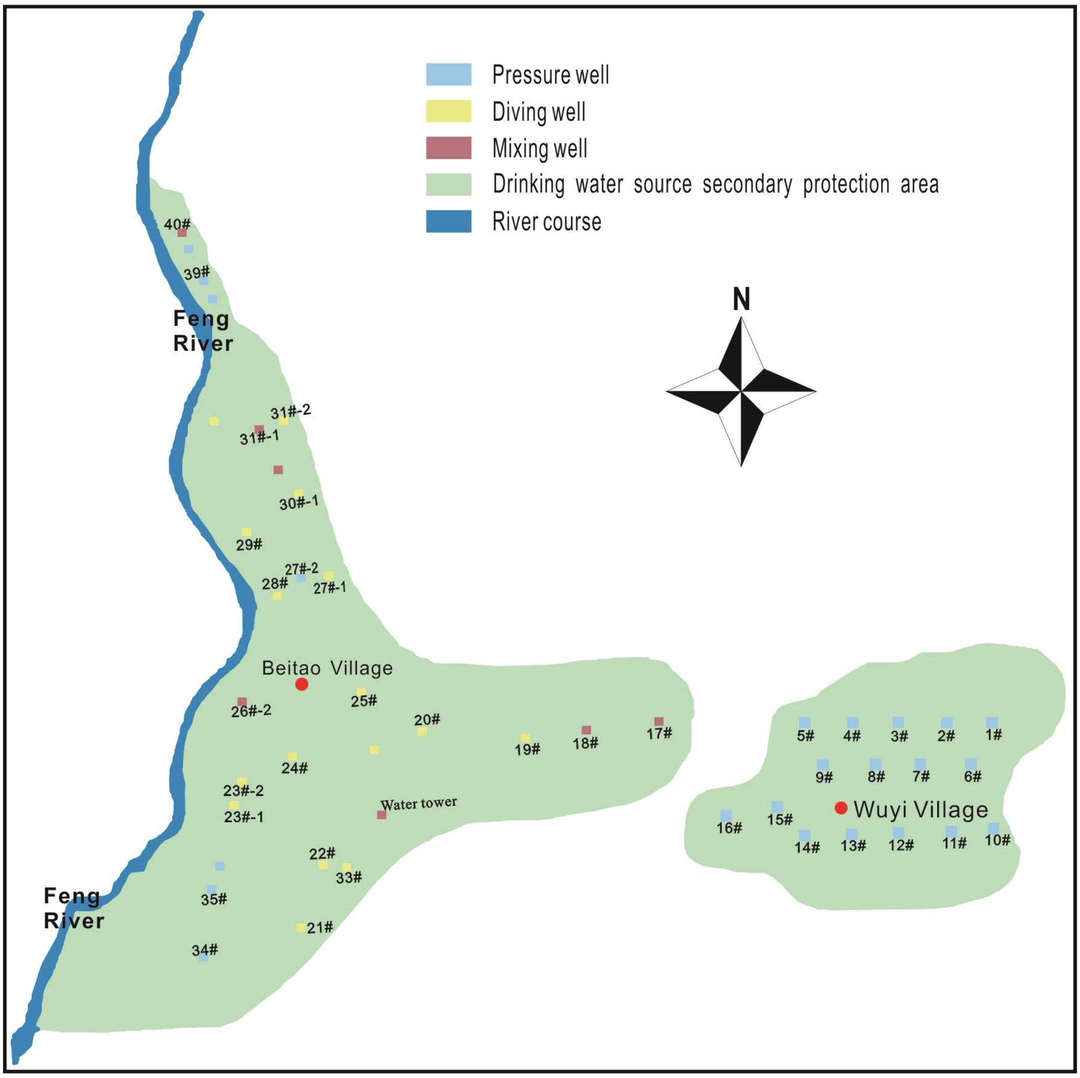


Figure 4. Geographical location of sampling point

Table 4. Testing methods and instruments used

Testing Indicator	Testing method	Testing base	Testing equipment
pH	Glass electrode method	GB/T 5750.4-2006	PHS-3C pH instrument
Total dissolved solids	Weighing method	GB/T 5750.4-2006	BSA224S Electronic balance
Total hardness	EDTA disodium titration method	GB/T 5750.4-2006	Acid burette
Ammonia Nitrogen	Nessler's reagent spectrophotometry	HJ 535-2009	Spectrophotometer UV9100A UV-visible spectrophotometer
Sulfide	Methylene blue spectrophotometry	GB/T 16489-1996	
Nitrate Nitrogen	UV spectrophotometry	GB/T 5750.5-2006	
Nitrite Nitrogen	Diazo coupling spectrophotometry	GB/T 5750.5-2006	
Sulfate	Barium Sulfate Turbid metric Method	GB/T 5750.5-2006	
Chloride	Silver nitrate volumetric method	GB/T 5750.5-2006	Acid burette
Iron, manganese, zinc, sodium, cadmium, lead	Inductively coupled plasma mass spectrometry	HJ 700-2014	7800 Inductively coupled plasma mass spectrometer

3.3 Evaluation criteria

According to the *China Groundwater Quality Standards* (GB/T14848-2017), specific classification standards for various indicators in different types of water quality(Table 5)：

Table 5. Groundwater quality standards

Serial number	Project \ Classification	Class I	Class II	Class III	Class IV	Class V
1	pH		$6.5 \le pH \le 8.5$		$5.5 \le pH < 6.5$ $8.5 < pH \le 9.0$	<5.5 >9.0
2	Total hardness (calculated as $CaCO_3$)	≤150	≤300	≤450	≤650	>650
3	Total dissolved solids	≤300	≤500	≤1000	≤2000	>2000
4	Sulfate	≤50	≤150	≤250	≤350	>350
5	Chloride	≤50	≤150	≤250	≤350	>350
6	Fe	≤0.1	≤0.2	≤0.3	≤2.0	>2.0
7	Mn	≤0.05	≤0.05	≤0.10	≤1.50	>1.50
8	Sulfide	≤0.005	≤0.01	≤0.02	≤0.10	>0.10
9	Zn	≤0.05	≤0.50	≤1.00	≤5.00	>5.00
10	Na	≤100	≤150	≤200	≤400	>400
11	Nitrate (N)	≤2.0	≤5.0	≤20.0	≤30.0	>30.0
12	Nitrite (N)	≤0.01	≤0.10	≤1.00	≤4.80	>4.80
13	Ammonia Nitrogen (NH_4^+)	≤0.02	≤0.10	≤0.50	≤1.50	>1.50
14	Cd	≤0.0001	≤0.001	≤0.005	≤0.01	>0.01
15	Pb	≤0.005	≤0.005	≤0.01	≤0.10	>0.10

Note：Except for the dimensionless pH, other units are mg/L.

3.4 Iron and manganese concentration statistics

Descriptive statistics of iron and manganese concentration in May, June and July of 13 single wells water in Feng underground water source area and mixed water before treatment by Xi'an No. 3 Waterworks (Table 6).

According to the water quality inspection in May, June and July, among the 15 indicators, the 7 indicators of pH、NO_3-N、Cl^-、Zn、Na、Pb and sulfide are all in Class I, indicating that these 7 indicators have an impact on groundwater quality. No effect; ；SO_4^{2-}、TDS、NO_2-N、Cd、NH_3-N and total hardness are all in the category I~III, indicating that these six indicators have little effect on groundwater quality.

The iron and manganese content in the mixed sample did not exceed the Grade III groundwater quality standard and the standard deviation and coefficients of variation were both less than 0.1, indicating that the iron and manganese content in the mixed water sample was relatively stable. In May, June and July, the evaluation grades of individual water samples exceeded Class III groundwater quality standards for the two indexes of Fe and Mn. There was 1 water sample with iron content exceeding the standard in May, 2 in June, and 1 in July. The highest value appeared In June 17# well; it exceeded the groundwater grade III water quality standard by 1.03 times. The iron content of 17# well exceeded the groundwater grade III water quality standard for 3 months. Although the average iron content of 19# well and 23-1# well was not Exceeding the groundwater level III water quality standard, but the content is high, the standard deviation and the coefficient of variation are small, indicating that the iron content of the 17#, 19# and 23-1# wells is stable, which has a great impact on the groundwater quality; the manganese content in May 3 There were 4 in June and 4 in July. The highest value appeared in the 19# well in June, which exceeded the groundwater quality standard by

3.92 times. The manganese content in the 17#, 19# and 27-1# wells in May, June and July all exceeded the groundwater quality standard in May, and the manganese content in the 23-2# well did not exceed the groundwater quality standard in May, but for 3 months The average value of, the standard deviation and the coefficient of variation are small, indicating that the 17#, 19#, 23-2#, and 27-1# wells have high manganese content, which has a great impact on groundwater quality.

Table 6. Statistics of iron and manganese concentration in groundwater of Feng River

	Well number	May	June	July	The average value	Standard Deviation	Coefficient of Variation
Fe(mg/L)	17#	0.302	0.312	0.307	0.307	0.004	0.013
	18#	0.108	0.197	0.203	0.169	0.043	0.257
	19#	0.295	0.301	0.284	0.293	0.007	0.024
	23-1#	0.271	0.297	0.258	0.275	0.016	0.059
	23-2#	0.131	0.182	0.171	0.161	0.022	0.136
	26-2#	0.112	0.167	0.182	0.154	0.030	0.196
	27-1#	0.229	0.243	0.209	0.227	0.140	0.061
	27-2#	0.161	0.256	0.264	0.227	0.047	0.206
	28#	0.132	0.198	0.217	0.182	0.036	0.199
	30-1#	0.152	0.182	0.139	0.158	0.018	0.114
	31-1#	0.152	0.213	0.225	0.197	0.032	0.163
	31-2#	0.143	0.185	0.181	0.170	0.019	0.112
	40#	0.081	0.241	0.236	0.186	0.074	0.399
	Mixed	0.241	0.229	0.204	0.225	0.015	0.068
Mn(mg/L)	17#	0.112	0.105	0.124	0.114	0.008	0.069
	18#	0.031	0.032	0.047	0.037	0.007	0.199
	19#	0.304	0.392	0.315	0.337	0.039	0.116
	23-1#	0.093	0.086	0.073	0.084	0.008	0.098
	23-2#	0.097	0.108	0.102	0.102	0.004	0.044
	26-2#	0.074	0.091	0.092	0.086	0.008	0.096
	27-1#	0.149	0.113	0.158	0.140	0.019	0.139
	27-2#	0.042	0.042	0.039	0.041	0.001	0.034
	28#	0.072	0.084	0.076	0.077	0.005	0.065
	30-1#	0.084	0.098	0.085	0.089	0.006	0.072
	31-1#	0.022	0.021	0.032	0.025	0.005	0.199
	31-2#	0.092	0.054	0.069	0.072	0.016	0.218
	40#	0.051	0.050	0.052	0.051	0.001	0.016
	Mixed	0.072	0.065	0.058	0.065	0.006	0.088

4. RESULTS AND DISCUSSION

The secondary protection zone of Feng River Water Source is dominated by rural residential land and river beach land. The water source protection area is 7.7km^2. The water source is divided into three lines: east, south, and north, and the surrounding environment are different. The east line is dominated by factories and the potential pollution sources are obvious; the surrounding environment of the south line protection area is relatively complicated. Most of the deep wells are located in residential areas with factories, Breeding farms and farmland, etc.; the environmental elements in the northern protection zone are relatively simple, and the surrounding areas of deep well are mainly residential areas. After investigation, it was found that there are no factories that directly produce and process iron and manganese or use iron and manganese for auxiliary production near the water source.

4.1 Influence of surface water infiltration on the concentration of iron and manganese in groundwater

The groundwater source of the Fenghe River is a riverside groundwater source. Iron and manganese in river water may also enter the groundwater body through the infiltration of the river to replenish the groundwater. Therefore, in order to study the relationship between the iron and manganese content in the Fenghe River water and the iron and manganese content in the groundwater, The water samples from the 17#, 19#, 23-2#, 26-2#, 30-1#, 31-2# pumped single wells and the water from the Fenghe River beside the single well were taken in May 2019, respectively. Samples were tested to analyze the relationship between iron and manganese content in groundwater and river water. The test results are as follows (Table 7).

Table 7. Iron and manganese content in single well and river water（mg/L）

	17#	19#	23-2#	26-2#	30-1#	31-2#	The average value
Iron in river water	0.013	0.018	0.004	0.005	0.027	0.031	0.016
Manganese in river water	0.012	0.041	0.010	0.007	0.069	0.011	0.025
Iron in well water	0.302	0.295	0.131	0.112	0.152	0.143	0.189
Manganese in well water	0.112	0.304	0.097	0.074	0.084	0.092	0.127

It can be seen from the table that the average iron and manganese content in the Feng River water are 0.016mg/L and 0.025mg/L, the average iron and manganese content in the groundwater are 0.189mg/L and 0.127mg/L, and the iron and manganese content in the Feng River are respectively 8.47% and 19.69% of groundwater, the iron and manganese content in river water is much lower than the iron and manganese content in groundwater, indicating that the iron and manganese content in Feng River water has no or little effect on groundwater and can be ignored. Therefore, this article considers iron and manganese in aquifers. The release may affect the iron and manganese content in groundwater. As the groundwater flows through the rock formations, the iron and manganese oxides in the rock mass gradually dissolve into the water body, which may cause the iron and manganese content in the water body to increase[19].

4.2 The content and distribution of iron and manganese in topsoil

In order to further explore the distribution of iron and manganese in the surface soil in the water source protection area, the surface soil next to the wells arranged from east to west and from south to north is used as the test object. After removing 30cm of the surface layer of floating soil, use the portable Niton tester Determine the content of iron and manganese in the soil.

In the research area, 17#, 18#, 19#, 20#, Water tower (W#), 25#, and 26# were selected in order from east to west in the study area. The surface soil next to the 7 wells was tested. The iron and manganese content in the surface soil was determined. The results are as follows (Figure 5).

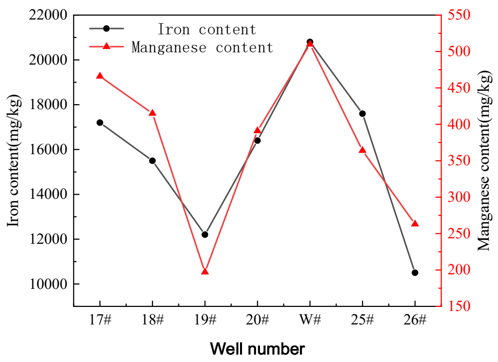


Figure 5. The east-west change law of iron and manganese content in surface soil

The manganese content can be seen from the figure, as the water source protection zone changes from east to west, the iron and manganese content in the surface soil changes uniformly, showing a trend of first decreasing, then increasing and then decreasing. The manganese content is the lowest at 19# well, at 26# the iron content in the well is the lowest, and both the iron and manganese in the water tower show the highest value. The iron content varies from 12200 to 20800 mg/kg, and the manganese content varies from 197 to 510 mg/kg. The measurement results are compared with Hu X F et al[20]. The results of determination of iron and manganese content in Shaanxi soil in the specificity of the palaeosoil formation process in the Loess Plateau are similar.

In the research area, 21#, 22#, 23#, 24#, 26#, 28#, 29#, 30#, 31#, and 40# are selected in order from south to north in the study area, and the surface soil next to 10 wells are selected as the test objects , Determine the content of iron and manganese in the surface soil, the results are as follows (Figure 6).

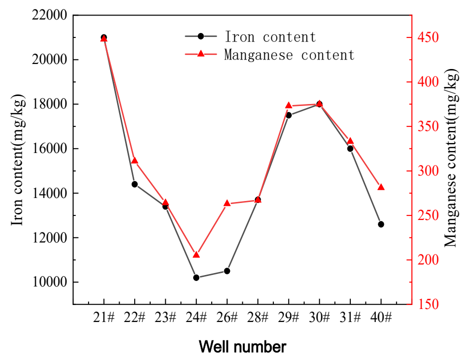


Figure 6. The north-south change law of iron and manganese content in surface soil

It can be seen from the figure that as the water source protection area changes from south to north, the change law of iron and manganese content in the surface soil is basically the same as the east-west change law. The iron and manganese content in the surface soil at the 21# well in the southernmost part of the water source protection area is the highest. They were 21,000mg/kg and 448mg/kg, and then moved northward, the iron and manganese content gradually decreased and reached the lowest point at 24# well. The iron and manganese content were 10,200mg/kg and 205mg/kg respectively and then gradually increased and then decreased. The range of iron and manganese content in the direction change is basically the same as that in the east-west direction. Iron and manganese in the soil may have some influence on the content of iron and manganese in groundwater.

4.3 Formation lithology and distribution of iron and manganese content

According to relevant literature, atlas and drilling data, the Quaternary Sediment in Xi'an City contains certain iron-manganese nodules, especially in the upper and lower 100m layers; a red-black iron-manganese film is common[21-23]. Use a portable Niton tester to test the iron and manganese content in the core taken from the borehole. The test is performed every 0.5m.

Since the iron and manganese content in the same formation with the same lithology is not much different, the iron and manganese content measured in a certain formation is used the average content indicates the iron and manganese content in the formation (Table 8).

It can be seen from Table 8 that the borehole location contains 33 layers of uneven thickness from 285.0m below the surface. The first 3.0m below the surface is plain fill and loess-like soil, with thicknesses of 1.7m and 1.3m, respectively, occupying a total of 1.1% of hole depth. The remaining 31 layers are silty clay, fine sand, medium-coarse sand and round gravel. Among them, there are 6 layers of silty clay, the thickness of a single layer is 0.5~5.5m, and the total thickness is 17.7m, accounting for 6.2% of the total drilling depth; there are 8 layers of fine sand, and the thickness of a single layer is 1.8~10.7m. The thickness is 40.7m, accounting for 14.6% of the total drilling depth; there are 11 layers of medium-coarse sand, with a large difference in single layer thickness. The minimum single layer thickness is 2.5m, the maximum single layer thickness is 59.5m, and the total thickness of the 11 layers is 192.0m, which exceeds the drilling depth. Half of the total depth of the hole, accounting for 67.4%; there are 6 layers of round gravel, the thickness of a single layer is not much different from the fine sand, which is 3.5~7.0m, and the total thickness is 31.1m, accounting for 10.9% of the total depth of the hole.

In rock masses of different lithology, the content of iron and manganese varies greatly. The content of iron and manganese in silty clay is generally higher, followed by the content of round gravel, and the content of iron and manganese in fine sand and medium-coarse sand is smaller. Generally speaking, the iron content in the rock mass in the study area is between 7065~24500mg/kg, the manganese content is content in the silty clay gradually increases as the depth of the formation increases, to the third between 119~562mg/kg, the highest iron content is 3.47 times the lowest content, and the highest manganese content is 4.72 times the lowest content .

The content of iron and manganese in the rock masses of different lithology in the strata 3~65m and 145~250m below the surface changes little. The content of iron and manganese fluctuates around 11000mg/kg and 200mg/kg respectively. The change of iron and manganese content is more obvious.

In general, if the adjacent stratum is composed of medium-coarse sand and fine sand, the change of iron and manganese content in the rock mass is smaller, or the content of fine sand is greater than that of medium-coarse sand, or the content of medium-coarse sand is greater than that of fine sand; When the stratum is composed of silty clay and fine sand, silty clay and medium-coarse sand, or silty clay round gravel, the iron and manganese content in silty clay is significantly higher than that in fine sand, medium-coarse sand and round gravel. ; If the adjacent stratum is composed of round gravel and fine sand or round gravel and medium-coarse sand, the iron and manganese content in the round gravel before 261m is higher than that in the fine sand and medium-coarse sand, and the iron and manganese content in the medium-coarse sand after 261m Higher than round gravel. In general, the iron and manganese content of rock masses of different lithology are silty clay>round gravel>fine sand and medium-coarse sand.

It can be seen from the table that there are 6 layers of silty clay in the drilling area, no silty clay layer appears in Q_4^{1al}, the first layer of silty clay appears in Q_2^{al}, 5 layers in Q_2^{al}, and 1 layer in Q_1^{al+l}. The iron and manganese content in the silty clay of the first layer of 40.0~41.3m is the smallest, 14,500mg/kg and 400mg/kg respectively, then the iron and manganese

layer of 74.8~78.2m. At the time, the iron and manganese content in the silty clay reached the maximum, respectively, the iron content was 24,500mg/kg and the manganese content was 562mg/kg. Subsequently, as the depth increases, the iron and manganese content in the silty clay gradually decreases in the Q_2^{al} formation. From Q_2^{al} to Q_1^{al+l}, the iron content in the rock mass increases slightly, and the manganese content increases significantly.

Table 8. Formation lithology change and iron and manganese content statistics table

Category	Depth（m）	Rock thickness（m）	Lithology	Fe（mg/kg） The average value	Fe（mg/kg） Standard error	Mn（mg/kg） The average value	Mn（mg/kg） Standard error
Shallow（0~30m）	0~1.7	1.7	plain fill	17600	184	368	7.84
	1.7~3.0	1.3	loess	21200	324	490	10.02
	3.0~7.8	4.8	Fine sand	9373	211	183	16.35
	7.8~15.0	7.2	Coarse sand	9215	509	199	6.01
	15.0~19.9	4.9	Round gravel	11089	297	288	22.98
	19.9~26.5	6.6	Fine sand	7458	607	141	14.62
	26.5~29.8	3.3	Coarse sand	7065	216	119	1.78
Middle level（30~100m）	29.8~36.1	6.3	Fine sand	9923	316	211	16.10
	36.1~40.0	3.9	Round gravel	10659	429	248	10.12
	40.0~41.3	1.3	Silty clay	14500	451	400	16.33
	41.3~52.0	10.7	Fine sand	13378	534	279	6.52
	52.0~65.0	13.0	Coarse sand	13204	111	254	4.33
	65.0~67.0	2.0	Fine sand	10465	263	215	1.93
	67.0~67.5	0.5	Silty clay	17366	123	471	14.15
	67.5~70.0	2.5	Coarse sand	13000	957	262	12.67
	70.0~74.8	4.8	Round gravel	16925	1283	354	8.99
	74.8~78.2	3.4	Silty clay	24500	1006	562	11.75
	78.2~80.0	1.8	Fine sand	12226	542	235	10.89
	80.0~92.9	12.9	Coarse sand	15700	335	321	14.74
	92.9~96.4	3.5	Silty clay	23412	817	465	18.68
	96.4~100.0	3.6	Coarse sand	13979	700	286	8.18
Deep（Below 100m）	100.0~142.0	42.0	Silty clay	13979	700	286	8.18
	142.0~145.0	3.0	Coarse sand	21150	840	424	10.59
	145.0~147.8	2.8	Round gravel	12400	670	215	7.14
	147.8~154.8	7.0	Coarse sand	13989	325	241	15.57
	154.8~179.5	24.7	Fine sand	10340	361	205	3.34
	179.5~184.0	4.5	Coarse sand	9003	289	192	8.73
	184.0~187.5	3.5	Round gravel	9092	303	209	5.27
	187.5~191.0	3.5	Coarse sand	11800	397	203	6.01
	191.0~250.5	59.5	Silty clay	8555	154	162	3.93
	250.5~256.0	6.0	Fine sand	21428	734	493	14.17
	256.0~261.0	5.0	Round gravel	9763	244	233	12.12
	261.0~268.0	7.0	Coarse sand	12281	325	260	11.35
	268.0~285.0	17	plain fill	16800	511	307	8.49

There are 11 layers of coarse sand in the borehole area, 1 layer in Q_4^{1al}, 9 layers in Q_2^{al}, and 1 layer in Q_1^{al+l}. The change trend of iron and manganese content in medium and coarse sand is similar, from Q_4^{1al} to Q2al content decreases, and the content is the lowest in the first layer 26.5~29.8m of Q_2^{al}, which is 7,065mg/kg and 119mg/kg, and then the iron and manganese content increases, in Q_2^{al} The iron and manganese content in the fourth layer of 80.0~92.9m reaches the maximum value in Q_2^{al}. Starting from the fourth layer in Q_2^{al}, the iron and manganese content gradually decreases until the last layer of Q_2^{al} and the ninth layer, from the ninth layer of Q_2^{al} to Q_1^{al+l}. The content of iron and manganese in medium-coarse sand increased significantly, and the content of iron and manganese in the 268.0~285.0m of Q_1^{al+l} reached the highest value of iron and manganese in medium-coarse sand, which were 16,800mg/kg and 307mg/kg respectively.

There are 6 layers of round gravel in the drilling area, 1 layer in Q_4^{1al}, 4 layers in Q_2^{al}, and 1 layer in Q_1^{al+l}. The change trend of iron and manganese content in round gravel is similar, from Q_4^{1al} to Q_2^{al} content decreases, the iron content is the lowest in the first layer 36.1~40.0m of Q_2^{al}, which is 10,659mg/kg, then the iron and manganese content increases, and the second layer of Q_2^{al} is 70.0 ~74.8m is the largest, 16,925mg/kg and 354mg/kg respectively. From the second layer of Q_2^{al}, the iron and manganese content gradually decreases until the last layer of Q_2^{al}. The fourth layer has the lowest manganese content, which is 203mg/kg. From the fourth layer of Q_2^{al} to Q_1^{al+l}, the iron and manganese content in the round gravel increased slightly.

In general, the iron and manganese content changes in the four different rock masses are basically the same. From Q_4^{1al} to Q_2^{al}, the iron and manganese content becomes smaller, and the

It can be seen from the figure that the iron and manganese content in the rock mass is positively correlated, R^2=0.89759, indicating that the two

iron and manganese content gradually increases from Q_2^{al}. In the middle and upper parts of Q_2^{al}, the iron and manganese content the content of iron and manganese is the largest, and then the content of iron and manganese gradually decreases to the lower part of Q_2^{al}. From the lower part of Q_2^{al} to Q_1^{al+l}, the content of iron and manganese in the rock mass increases, and the content of iron and manganese in medium coarse sand increases most obviously.

According to the data in the table, establish the SPSS data file and analyze the correlation of the iron and manganese content in the rock mass. The results are shown in Figure 7.

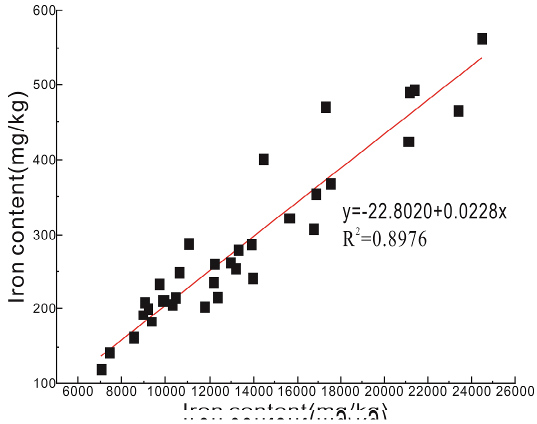


Figure 7. Correlation of iron and manganese in rock mass

There are 8 layers of fine sand in the drilling area, 1 layer in Q_4^{1al}, 6 layers in Q_2^{al}, and 1 layer in Q_1^{al+l}. The change trend of iron and manganese content in fine sand is similar, decreasing from Q_4^{1al} to Q_2^{al}. The iron and manganese content in the first layer 19.9~26.5m of Q_2^{al} is the smallest, 7,458mg/kg and 141mg/kg, respectively, and then the iron and manganese content increases. The iron and manganese content in the three layers 41.3~52.0m is the largest, 13,378mg/kg and 279mg/kg, respectively, and then the iron and manganese content fluctuates. In the last layer of Q_2^{al} from 179.5 to 184.0m to Q_1^{al+l}, the content of iron and manganese increases.

elements of iron and manganese in the rock mass have a relatively close genetic relationship.

4.4 Evaluation of factors affecting the release rate of iron and manganese in groundwater in

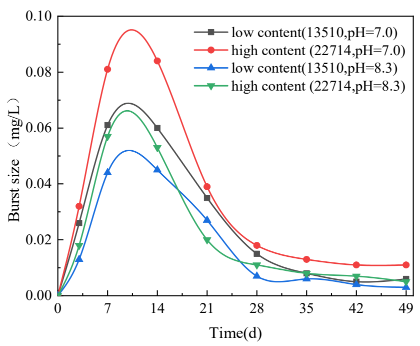
rock and soil

Two representative layers of silty clay, fine sand, medium-coarse sand, and round gravel were selected at the drilling site, among which silty clay was selected at 41m and 77m, fine sand was selected at 50m and 180m, and medium-coarse sand was selected at 100m. At 160m and 38m, round gravel was selected at 38m and 72m. After sampling in a sealed bag, it was transported back to the laboratory to determine the release rate of iron and manganese in the core.

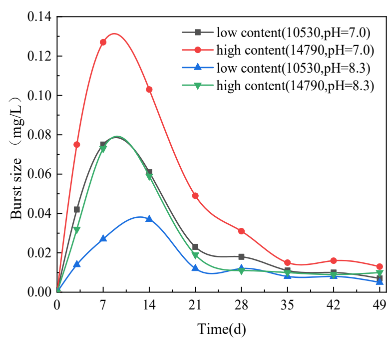
Before measuring the iron and manganese content in the cores taken, the cores were placed on a plastic sheet in a ventilated room to dry in the shade. When the core is half dry, mash the large pieces, especially the silty clay, to avoid forming hard lumps that are difficult to grind or dry completely after being completely air-dried, and pay attention not to cause soil pollution during the mashing process. After air-drying, pour it into a mortar and grind finely, and pass it through a 100-mesh sieve for testing. When determining the iron and manganese content in the core, the finely ground core is digested. The specific method is as follows: weigh 0.5g sample into a 25mL PTFE crucible, wet with a small amount of water, add 10mL hydrochloric acid, and control the temperature of the electric heating plate Heat and dissolve at a low temperature for 2 hours at 100°C, continue to add 15mL nitric acid and heat until the remaining liquid in the crucible is 5mL, add 5mL hydrofluoric acid to heat to decompose silicon oxide and colloidal silicate, and finally add 5mL per chloric acid and heat to evaporate. After removing the crucible, cool it slightly, dissolve the residue with 1mL (1+5) nitric acid solution, transfer it to a 25mL volumetric flask, and shake it to a constant volume after cooling. The content of iron and manganese in the filtered solution was measured by inductively coupled plasma mass spectrometer, and the content of iron and manganese in the measured solution was converted into the content of iron and manganese in the core.

Said take 20.0 g iron manganese content in different dry fine grinding of silty clay and fine sand, coarse sand and gravel in the gravel in the conical flask, add 100 ml of deionized water as in overlying water, because most of the pH of the groundwater in the study area is weak alkaline, neutral minority, in order to ensure the close to the actual situation, so the pH value of 7.0 and 8.3 at room temperature under the condition of iron and manganese content in different rock mass measurement silty clay and fine sand, coarse sand and gravel iron and manganese release.

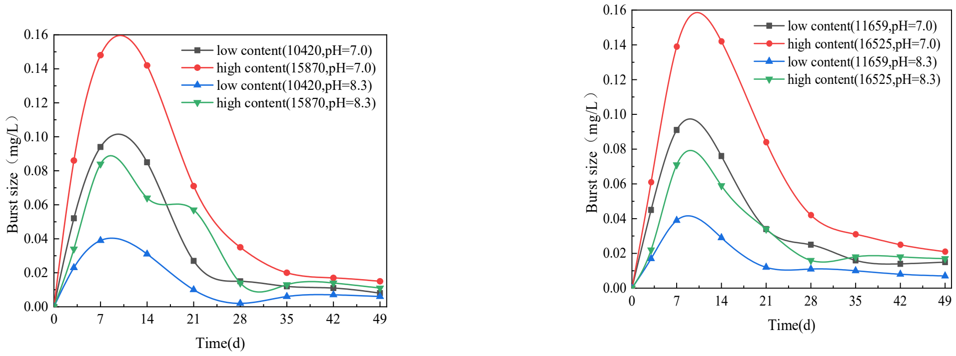
The law of iron release in four different rock masses of silty clay, fine sand, medium coarse sand and round gravel is shown in the figure 8.



（a）The release of iron from silty clay



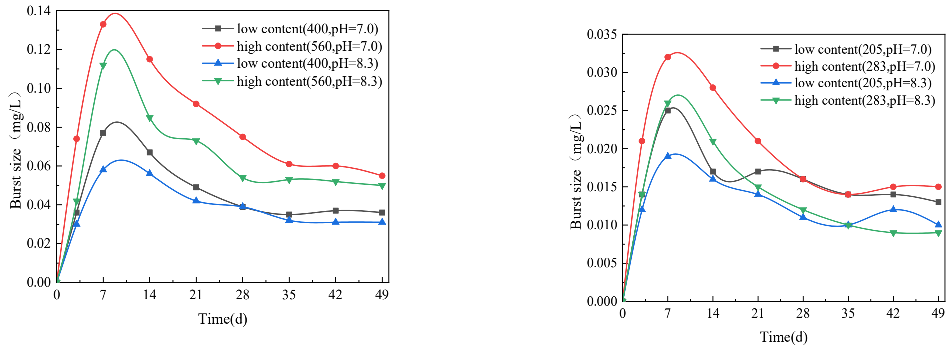
（b）The release of iron from fine sand



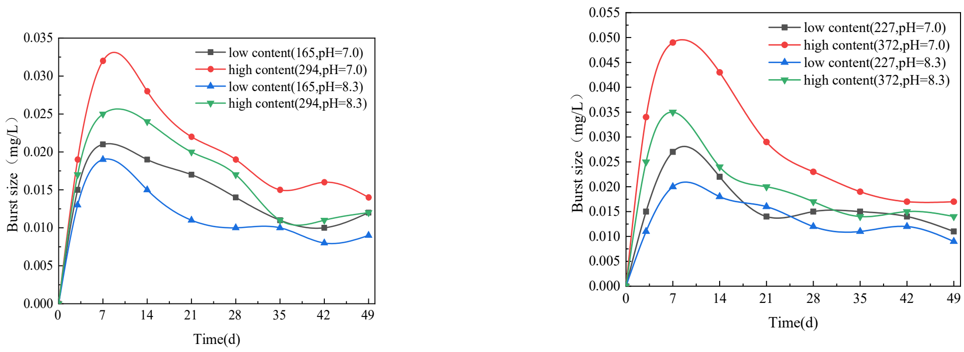
（c）The release of iron from medium coarse sand　　（d）The release of iron from boulders

Figure 8. The release of iron in different rock masses

The release regularity of manganese elements in the rock mass of silty clay, fine sand, medium coarse sand and round gravel is shown in the figure 9.



（a）The release of manganese from silty clay　　（b）The release of manganese from fine sand



（c）The release of manganese from medium coarse sand　　（d）The release of manganese from boulders

Figure 9. The release of manganese in different rock masses

As can be seen from the figure, when the pH is smaller, the iron and manganese elements are released from the rock mass faster, and the content measured in the overlying water is higher. This is mainly because when the alkalinity is stronger, the more OH· free state in the groundwater is, which leads to the reaction of low-priced Fe and Mn soluble salts with OH^- to form high-priced sediments $Fe(OH)_3$ and MnO_2.The equation is as follows:

$$Fe^{2+} + OH^- \longrightarrow Fe(OH)_3\downarrow$$

$$Mn^{2+} + O_2 + H_2O \longrightarrow MnO_2\downarrow + H^+$$

The research area is near farmland, and the application of pesticides and fertilizers has a long-term effect on groundwater. This is mainly due to the changes in the pH environment caused by the input of man-made pollutants and the changes in the REDOX environment caused by the decomposition of organic matter in pollutants under the action of microorganisms and the production of reducing substances such as carbon dioxide and hydrogen sulfide. The high iron and manganese oxides which are difficult to dissolve are reduced to low iron and manganese soluble salts, which eventually leads to the continuous increase of iron and manganese content in groundwater[8]. The equation is as follows:

$$Fe(OH)_3 + CH_2O + H^+ \longrightarrow Fe^{2+} + HCO_3^- + H_2O$$

$$Fe_2O_3 + CH_2O + H^+ \longrightarrow Fe^{2+} + CO_2 + H_2O$$

This phenomenon is also consistent with the change trend of pH and Eh in this region.

5. CONCLUSIONS

(1) The western suburbs of xi 'an of shallow groundwater quality overall is good, but there are still a part of the well water III class Fe and Mn content in water quality standards. Excess water mainly comes from the diving well, including iron content is 1.03 times most superb III class water quality standard, manganese content in the most superb III class 3.92 times water quality standards. Super III class water samples respectively, accounting for 9.5% of the total sample points, to 26.2%.The high value point is located far away from the river and close to the farmland. The infiltration supply at this point is weak and shows strong reducibility, which is conducive to the generation of low iron and manganese salts and more difficult to be diluted with underground runoff.

(2) River near the underground water source, there is no direct production and processing of iron and manganese companies and factories, the average iron manganese content in the river water were 0.016 mg/L and 0.025 mg/L, the average iron manganese content in groundwater were 0.189 mg/L and 0.127 mg/L, the river water Fe and Mn content are respectively 8.47% and 19.69% of the groundwater, so the river groundwater individual well higher levels of iron, manganese and no obvious contact.

(3) The content of iron and manganese in the rock mass in the study area is 7,065~24,500mg/kg, and 119~562mg/kg. The content of iron and manganese in the rock mass of different lithology is powdery clay > boulder gravel > fine sand and medium coarse sand. The same lithology of Fe and Mn content change rule of rock mass basic same, Fe and Mn content decreases from Q_4^{1al} to Q_2^{al} strata, starting from the Q_2^{al} iron manganese content gradually increased, in Q_2^{al} upper iron and manganese content in the biggest, then gradually become smaller, iron and manganese content from lower Q_2^{al} to Q_1^{al+1} Fe and Mn content increasing, the rock mass in the coarse sand Fe and Mn content is most obvious. Meanwhile, the content of iron and manganese in rock mass is positively correlated, R^2=0.89759, and these two elements in rock mass have a close genetic relationship.

(4) The release law of Fe and Mn in rock mass of different lithology is basically the same. In the overburden water, Fe and Mn all go through three stages of rapid increase, fall and tend to be stable. When the final release tends to be stable, the release rate of manganese in rock mass is higher than that of iron. The manganese content in overlying water is 0.010~0.057mg/L, the release rate is 0.02%~0.05%, and the iron content is 0.004~0.023mg/L, the release rate is

less than 0.01%. Meanwhile, the inhibition effect of higher pH in water environment on the release of iron in rock mass is significantly higher than that of manganese.