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The characteristics of hydrogeochemical zonation of groundwater in inland plain

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Abstract To find out the hydrochemical zoning of groundwaterin the inland plain, taking Jiyang plain as an example, based on mathematical statistics, ion ratio coefficient and isotopic analysis method, the characteristics of water chemical composition and its zoning at different depths of 500m were studied.The result shows: ①The groundwater flow system in the study area can be divided into local flow system, intermediate flow system and regional flow system. ②The hydrochemical type of shallow groundwater is complex. The hydrochemical types of middle confined water are mainly $Cl\cdot SO_4$—$Mg\cdot Na$ and $SO_4\cdot Cl$—$Na\cdot Mg$. The deep confined water is mainly HCO_3. ③The TDS of shallow groundwater increases gradually along the direction of groundwater flow. ④The shallow saltwater and freshwater are alternately distributed in horizontal direction, and saltwater is distributed sporadically in the interfluve area with sporadic punctate or banded, and hydrochemical types are mainly $Cl\cdot SO_4$—$Na\cdot Mg\cdot Ca$. Conclusion: Groundwater in the study area is affected by complicated hydrogeochemical action, mainly in the form of filtration, cation exchange and evaporation. The inland plain area is characterized by hydrogeochemical zonation in horizontal and vertical.

1. Introduction

The hydrogeochemical characteristics of groundwater are important components of hydrogeochemistry, which are of great significance for the exploitation and utilization of groundwater resources (AN et al. 2012). In the flow process, groundwater and surrounding medium continuous mass exchange, whose chemical composition changes with time and runoff, so the chemical characteristics of the groundwater are affected by many factors, such as topography, geological background, hydrodynamic field and human activities. Chemical composition is the result of long-term interaction between groundwater and its surrounding environment. In the process of groundwater flow, hydrogeochemical action and it's intensity change, and the different hydrogeochemical processes lead to the difference of chemical composition of groundwater. It shows that the hydrochemical composition or salinity changes regularly in the horizontal and vertical directions, namely the hydrogeochemical belt(Li et al.2017; Marina and Olga 2016). Therefore, hydrochemical characteristics can reflect the hydrogeochemical process well, and it is an important basis for dividing the horizontal and vertical zoning of hydrogeochemical level(Sun et al 2016; Feng and Zhang 2014). Mathematical statistics, ion ratio coefficient and mineralizer saturation coefficient have been widely used in the study of hydrogeochemical zoning(Oumar et al. 2015; Xing et al. 2015). Previous studies are mostly concentrated on the chemical zoning of groundwater and water in the basin and coastal shallow layer, while the hydrogeochemical zoning in the inland plain is less(AN et al 2012; Luan et al. 2016).

The water resources are short in the north of the Yellow River, and the overexploitation of

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groundwater has caused many hydrogeological problems. The extensive TDS>2g • L^{-1} salt water has not been fully utilized. Therefore, taking Jiyang plain as an example, based on long-term monitoring of groundwater dynamics, stratified sampling and routine ion composition test of groundwater, the hydrogeochemical zoning characteristics of groundwater were studied by mathematical statistics, ionic proportion coefficient and isotopic analysis methods, so as to provide scientific basis for the evolution of saline and freshwater.

2. Study area

Terrain decreased from southwest to northeast in the study area, and the terrain gradient is 1/7000-1/8000(Figure 1). The groundwater hydraulic gradient leads to slowly motion, saltwater is widely distributed(Xing et al. 2015). From the paleogeography and paleoclimate, it is influenced by the frequent alteration of the Yellow River and the distribution of the ancient river channel. The alluvial lacustrine product coexist, and the sedimentary environment is complex. The depth of 500m in the study area is divided into three aquifers: buried depth less than 40 m is the submersible aquifer, whose lithology is mainly silt, fine sand. The buried depth of 60 m-200 m is the medium confined water, whose lithology is mainly silt sand and medium fine sand. The diving water and medium confined water are separated by the weak permeable layer. The buried depth of the top plate in 200-300 m and the bottom depth of 450-500 m is the deep confined water, whose lithology is mainly medium sand and fine sand.

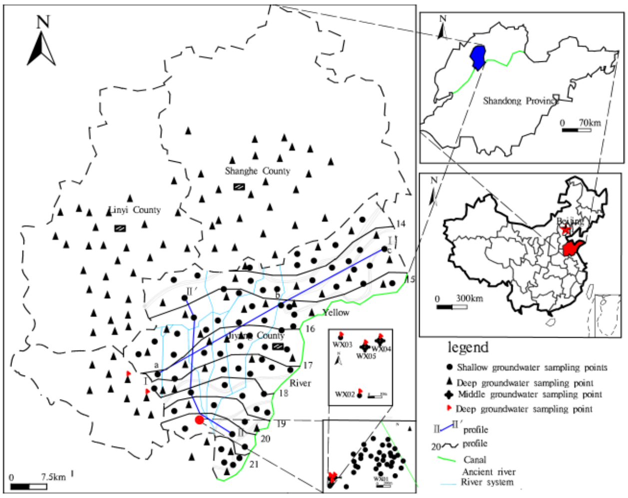

Figure 1. The sketch map of groundwater flow field and sampling point in study area

3. Medthod

3.1 Sample Collection

The study area is located in Jiyang Plain(1076 km^2), where 70 samples of shallow groundwater and 40 samples of middle confined water are collected, and 101 deep groundwater water samples is coming from Jiyang county and its surrounding areas, taking 10 different depth isotope water samples. At the same time, 20 samples of shallow saltwater were collected from typical saltwater area(3.2km^2). The hydrogeological investigation of typical saline water area shows that 321 m is mainly composed of clay, silty clay and local silty sand interlayer. Drilling for WX01, WX02, WX03, WX04, WX05, WX06, six stratified water stop observation wells (Table 1). 2 years' dynamic monitoring is carried out to obtain the water level and water quality data of different depth aquifers.

Table 1. Basic parameters of typical test wells

number	Drill diameter/mm	Well completion depth/m	Aquifer location/m	well water level elevation/m	Permeability coefficient/（m·d-1）	Aquifer lithology

WX01	146	8	3.0 — 8.0	23.587	0.835	silty clay
WX02	146	12	8 — 11.6	21.027	0.145	silt
WX03	235	50	13 — 50	20.985	0.355	silty clay
WX04	140	91	78 — 90	19.157	0.037	silty clay
WX05	140	113	99 — 107	18.26	0.453	Silty sand
WX06	180	336.66	274 — 333	24	1.964	Fine sand, fine sand, medium sand

3.2 Sample Testing

Test items: K^+, Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^-, pH and total dissolved solids (TDS). Use PXSJ-216F ion meter(resolution ratio 0.0001, error 0.3%) to test K+ and Na+. EDTA continuous titration is for the determination of Ca^{2+} and Mg^{2+}. SO_4^{2-} test by EDTA-Mg titration. The HCO_3^- and CO_3^{2-} test methods are acid-base titration, methyl orange as an indicator. The Cl^- test method is silver titration, and the indicator is potassium chromate. The total dissolved solids (TDS) is the sum of the ion mass concentrations. The relative error of ion balance in all water samples is less than 5%, all of whom are reliable data.

The ^{14}C, ^3H sample is sealed in a glass bottle and stored without light. Send to Beta Analytic Radiocarbon Dating Laboratory to complete the test.

4. Results and Discussion

4.1 The characteristics of water chemical horizontal zoning in groundwater

The type of shallow hydrochemistry shows a certain horizontal zonation, which shows as follows:

1) Groundwater flow is a northeast-southwest. and TDS increased along the way of groundwater flow. The average TDS in the study area was 1684.94 mg/L. The TDS in the southwest was lower, and the average was only 1003 mg/L. The average TDS was 1452.3mg/L in the middle part, and the TDS in the northeast was higher with an average value of 2486.6 mg/L. Along the routeI—I'(Figure 1), the Southwest (a) - (b)Central - Northeast (c), from TDS <1g/L freshwater into TDS>3g/L saltwater(Figure. 2). The hydrochemical types are HCO_3—Na·Mg, HCO_3·Cl·SO_4—Na·Mg, Cl·HCO_3—Na·Mg.

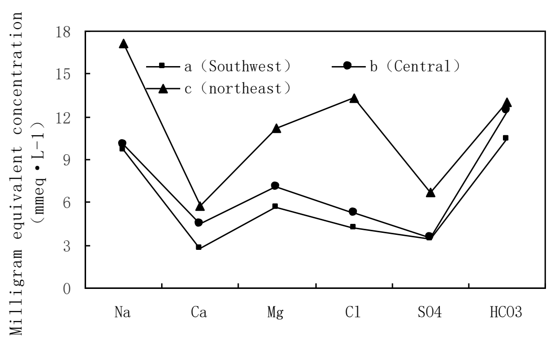

Figure 2. The variation trend of shallow groundwater component content

2) Saltwater and freshwater are distributed internating at local. The saltwater shows a sporadic or irregular strip distribution. Jiyang County surface water system more developed, the Yellow River, Tu Hai River flows through the territory. From the two sides of the river, the ancient river road to the inter-river zone, the shallow groundwater changed from freshwater to brackish water or saltwater. Fig.1 Section Ⅱ-Ⅱ' of section, the hydrochemical types are HCO_3 • Cl—Mg • Na • Ca, Cl • SO_4—Mg • Na • Ca, HCO_3 • Cl—Mg • Na, HCO_3 • Cl—Mg • Na, Cl • SO_4—Na • Mg, forming a pattern of brackish water phase distribution.

4.2 Vertical zoning characteristics of groundwater hydrochemistry

The chemical types of shallow groundwater are complex, ranging from TDS < 2 g/L to TDS>10g/L (Table 2). There are 43 types of hydrochemistry, of which TDS < 2g/L freshwater accounts for 74.3%, mainly HCO_3—Na (Na • Mg, Mg • Na). The brackish water of 2~3g/L accounted for 15.7%. The main hydrochemical types were Cl •HCO_3 (HCO_3 •Cl •SO_4) —Na •Mg, HCO_3—Na(Na •Mg), HCO_3 •SO_4 —Na. 3 ~ 5g/L brackish water accounted for 8.6%. The hydrochemistry type was mainly Cl • HCO_3— Mg •Na •Ca, followed by Cl •SO_4—Na •Mg. TDS>5g/L saltwater is Cl •SO_4—Na •Mg (Mg •Na •Ca). The salinity of shallow saltwater in typical saltwater area is higher than 10g/L. The concentration of cation Na^+ is the highest (2029.10 mg/L), followed by Ca^{2+} and Mg^{2+}. The concentration of anion Cl^- is the highest (3791.6 mg/L), and the main hydrochemical types are Cl •SO_4—Mg •Na •Ca. The HCO_3^- concentration in shallow groundwater is high and the coefficient of variation is small, indicating that HCO_3^- is relatively stable. Cl^-,SO_4^{2-},Na^+ larger coefficient of variation, resulting in a complex chemical type of water.

Table 2. The characteristic values of conventional hydrochemical composition of groundwater (n=141)

	Index	Na^+	Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}	Cl^-	TDS
Unconfined water (n=70)	Maximum	1785.2	1021.6	1202.0	1296.3	2928.4	5321.2	13096.5
	Minimun	52.2	39.4	31.4	58.6	4.0	22.8	549.9
	Average	256.6	110.0	103.1	667.5	284.0	263.7	1684.9
	Coefficient of variation（%）	80.1	46.0	63.3	36.8	94.8	99.5	55.6
Middle confined water (n=20)	Maximum	2250.2	879.3	853.2	318.1	3266.2	3616.5	13482.3
	Minimun	1088.2	395.3	336.7	192.3	849.0	849.1	5572.8
	Average	2108.0	545.1	560.9	244.7	3266.2	2 865.5	8991.5
	Coefficient of variation（%）	29.3	25.4	29.8	17.9	58.1	9.1	31.0
Deep confined water (n=101)	Maximum	970.0	125.2	110.9	540.0	1274.0	1036.3	3339.8
	Minimun	11.0	5.2	1.3	186.2	16.9	21.5	372.7
	Average	345.3	27.6	23.7	429.0	206.0	247.6	1285.1
	Coefficient of variation（%）	34.6	91.6	76.7	26.1	74.9	59.0	28.2

Note: The indicator unit is (mg /L)

The middle confined water is TDS > 5g/L saltwater, and the average concentration of cations is as follows: Na^+>Mg^{2+}>Ca^{2+}. The average mass concentration of anions was as follows: SO_4^{2-}>Cl^->HCO_3^-. Except for SO_4^{2-}, the other conventional ion coefficient of variation is small, and the hydrochemical type is mainly SO_4 • Cl (Cl • SO_4)— Na • Mg.

The deep confined water was TDS < 3g/L. The concentration of cationic Na^+ was the highest. The average value was 345.3 mg/L. The mass concentration of the anion HCO_3^- (429.1 mg/L) was the highest, followed by Cl^-, SO_4^{2-}. The coefficient of variation of HCO_3^- and Na^+ was small, and the hydrochemical type was mainly HCO_3 type, including HCO_3—Na, HCO3 • Cl(HCO_3 • SO_4 • Cl, HCO_3 • Cl • SO_4)—Na, and some samples are Cl • HCO_3 • SO_4—Na, HCO_3—Ca • Mg.

The vertical zoning of hydrochemical types in the study area is divided into three types (Figure 6): ①The hydrochemical type of unconfined groundwater and deep confined goundwater is HCO_3 type, and the middle confined groundwater is Cl • SO_4 or SO_4 • Cl type; ②Due to the low lying land, it belongs to the groundwater system converge area. The shallow layer forms Cl •SO_4 type, and the lower part of its hydrochemical type is HCO_3 or HCO_3 •Cl type, Cl •SO_4 or SO_4 •Cl type and HCO_3 type. The shallow saltwater is connected with the middle saltwater, and the hydrochemical type are Cl • SO_4 or SO_4 • Cl type and HCO_3 type, such as Xiyan Village, Sungeng.

4.3 The characteristics of hydrochemistry reveal classification of flow system

4.3.1 Classification of flow system

The dynamic characteristics of different groundwater level are different. The unconfined groundwater level is mainly affected by the mixing effect of precipitation and irrigation infiltration. The dry season drops and the rainy season rises. The water level of the medium confined water is relatively stable. The deep confined water is affected by artificial exploitation, whose level continues to decline (Figure 3).

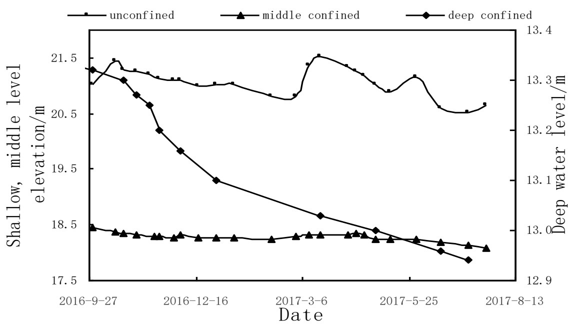

Figure 3. Dynamic feature map of groundwater level at different depths

The PIPER trilinear chart shows that the driving samples are concentrated in the 5 zone with carbonate hardness over 50%, the 7 zone where alkali and strong acid are dominant, and the 9 zone in which the anion and anion contents of any pair are not more than 50%. The middle confined water sample is in the 1 zone where the alkali earth metal ion exceeds the alkali metal ion and the 4 zone where the strong acid is larger than the weak acid. More than 3/4 deep confined groundwater samples are located in the lower half of the 2 zone, while driving water is only 2.8% in the lower half of the 2 zone (Figure 4). There are differences in the chemical characteristics of unconfined groundwater, middle and deep confined groundwater. The age of shallow groundwater determined by ^{3}H is 30-50a, The age of WX04 and WX05 measured by ^{14}C were 39010 a and 36150 a respectively. In Qihe County, the depth of deep groundwater is about 200m, and the groundwater age of buried depth of 300 m and 400 m is 16247 a and 13651 a, respectively (Yang et al. 2009). Combined with different groundwater dynamic characteristics, groundwater age and hydrochemical characteristics, it shows that shallow, middle and deep layers groundwater belong to different groundwater flow systems. Unconfined groundwater belongs to the shallow local flow system, and the middle confined groundwater belongs to the middle flow system, and the deep confined water belongs to the deep regional flow system.

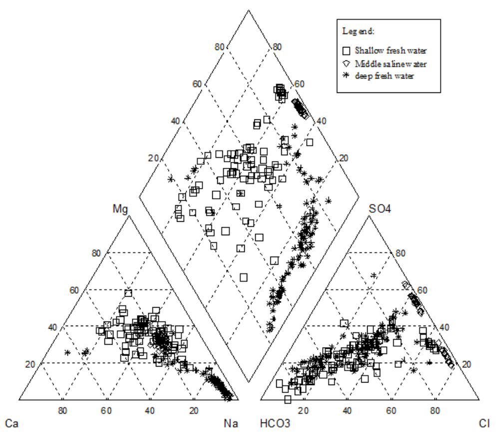

Figure 4. Piperdiagram for unconfined water—middle confined water—deep confined water

4.3.2 The ion ratio coefficient reveals hydrogeochemical action

Filtration effect: γ Na/ γ Cl as a sign of leaching and accumulation of strength, is the genetic coefficient of groundwater(Xing et al. 2015). The γ Na/ γ Cl of unconfined groundwater in 1~2 occupies 55.7%, and the coefficient of γ Mg/ γ Ca is 1~2, far less than that of seawater standard 5.5, indicating that the composition of groundwater is closely related to the filtration effect.

Cation exchange: The shallow saltwater γ Na/ γ Cl in typical saltwater area is 0.5~0.6, and the middle confined water γ Na/ γ Cl range is 0.45~0.8, which is lower than that of filtration water. The higher γ Na/ γ Cl corresponds to the lower γ Mg and γ Ca (Figure 5), and the cation exchange may occur. γ Ca/ γ Na and γ Mg/ γ Na are used to determine the intensity of ion exchange reactions in water chemistry (Feng and Zhang 2014). The typical salt water area γ Mg/ γ Na> 1, γ Ca/ γ Na <1, the cation exchange effect is more intense, Mg^{2+} is in a dominant position.

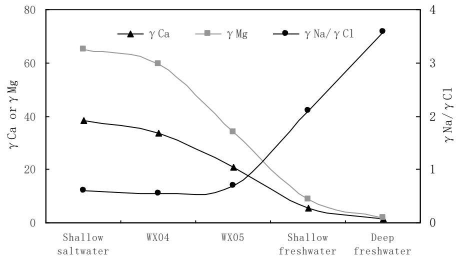

Figure 5. γ Mg, γ Ca and γ Na/ γ Cl of different types of groundwater

Evaporative concentration: γ Ca/ γ Cl is a parameter describing the hydrodynamic conditions (Marina and Olga 2016). The smaller the coefficient of γ Ca/ γ Cl is, the worse the hydrodynamic condition is. When the shallow groundwater is TDS < 1.2g/L, γ Ca/ γ Cl> 2, and the runoff conditions are good. When TDS > 3g/L, γ Ca/ γ Cl < 0.6, and the runoff condition is poor. The typical saltwater zone γ Ca/ γ Cl ranged from 0.2 to 0.4, with very poor hydrodynamic conditions and consistent with the small hydraulic gradient and slow runoff. The concentration of Ca^{2+} in shallow saltwater of typical saltwater zone is high, reaching 908.89 mg/L, higher than the average concentration of 109.97 mg/L. The saltwater concentration is affected by evaporation.

γ HCO_3/ γ SO_4, γ HCO_3/ γ Cl and γ SO_4/ γ Cl are hydrogeochemical parameters used to represent the evolution of anions and the compositional distribution ratio. The mean value of the coefficient of γ HCO_3/ γ SO_4 and γ HCO_3/ γ Cl for dives is about 5.3 and 2.7, mainly from carbonate dissolution. The coefficients of γ HCO_3/ γ SO_4 and γ HCO_3/ γ Cl in the shallow and middle confined groundwater were both less than 1, mainly due to the dissolution of evaporite. The soluble salt is easy to accumulate, and the water body tends to be salty. The variation range of SI_C and SI_D is 0.66-1.16 and 0.56-2.58, and calcite and dolomite are in the state of supersaturation, and decarbonation may occur.

4.4.3 Genetic analysis of hydrochemical zonation

The study area belongs to the Yellow River flood plain, and the shallow local flow system is recharged by atmospheric precipitation with a strong leaching effect. However, due to the small hydraulic gradient and slow runoff in the Jiyang plain, under the effect of evaporation, the hydrochemical types are complex. Both sides of the river receive lateral recharge of the river, and sedimentary lithology of the ancient river channel is coarser, whose watery is good, and the TDS of the groundwater is lower. The inter-river basin is poorly water-rich and low-lying, affected by the gravitational potential, and groundwater in high terrain migrates to lower-lying inter-river areas and forms a local mobile system sink. The groundwater is buried shallowly, which lead to form shallow salty Water(Figure 6). The chemical characteristics of deep confined groundwater are different from that of shallow groundwater, and the ionic ratio coefficient reflects that the deep confined water is subject to cation exchange. Middle confined groundwater age of 39-36 ka B.P. And 54-30kaB.P. Interglacial to glacial transitions, warm and dry climate, strongly evaporation led to the formation of middle-saltwater. Ion ratio coefficient, saturation coefficient reflects that the middle salty water is affected by cation exchange.

The middle confined water level is stable at 18-18.5 m, the deep confined level is 12.9-24 m, the head difference between middle confined water and deep confined water is always small, the vertical exchange effect is weak. The low rate of development and utilization of middle confined groundwater, due to the high head, upward migration in low-lying terrain to form a local saltwater, similar to the Sungeng town. Topography, sedimentary environment, paleoclimatic geography, hydrodynamic conditions and other factors cause the complexity of groundwater hydrochemical characteristics.

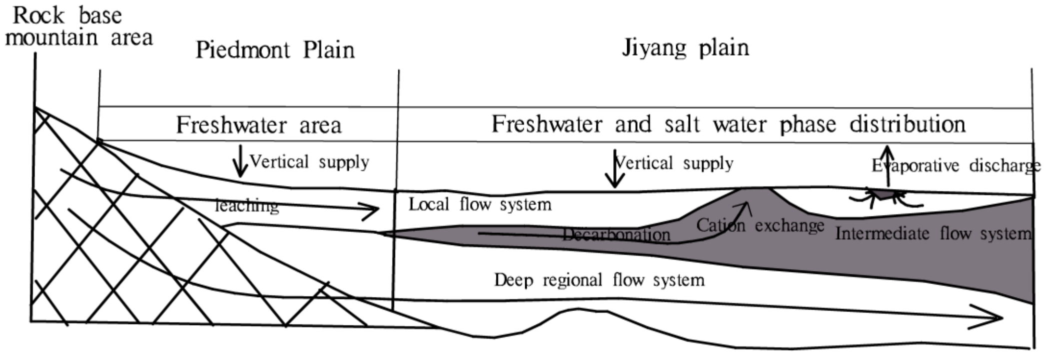

Figure 6. the schematic diagram of groundwater flow system and hydrochemical action

5. Conclusion

(1) Affected by hydrodynamic conditions, sedimentary environment and topography, the TDS of shallow groundwater in the inland plain area gradually increases along the groundwater flow direction. The fresh and saltwater distributes horizontally in the horizontal direction. The saltwater shows sporadic or irregular bands. High-salinity shallow saltwater mainly distributes in interfluve. The low salinity shallow fresh water mainly distributes on both sides of rivers and ancient rivers.

(2) The hydrochemical types of shallow groundwater are complex. The middle level confined water is mainly Cl • SO_4-Na • Mg, SO_4 • Cl—Na • Mg, and the properties are relatively stable. Deep fresh water is mainly HCO3 type.

(3) The groundwater in the study area is affected by complex hydrogeochemistry such as leaching, cation exchange and evaporation. In the inland plains, there are horizontal and vertical hydrogeochemical zonation characteristics.

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