https://doi.org/10.1051/e3sconf/202129002014

Hydrochemical Characteristics and Evolution Laws of Shallow Groundwater in Shuangliao City

Li Xuguang[1], Zhao YanDai[1,*], He Haiyang[1]

[1]Shenyang Center of Geological Survey, China Geological Survey, Shenyang,Liao Ning, China

Abstract. Shuangliao City is an important part of the Xiliaohe Plain, and one of the most important bases of grain production in the north of China. Therefore, it is important to ascertain the hydrochemical characteristics of groundwater and their causes and evolution laws in the Xiliaohe Plain to provide guidance to agriculture development and ecological improvement. After collection of detailed data and identification of the groundwater flow field, we studied the causes and evolution of the identified hydrochemical types by zone with mathematical statistics, correlation analysis, ion proportional coefficient and other methods. The results show that the concentrations of HCO3-, Cl-, and Na+ are relatively high, and these of Ca2+, Mg2+, SO42-, and NO3- are relatively low. The concentration of TDS increases gradually along the flow direction of groundwater, and TDS is positively correlated to the variation in concentration of Cl-, Na+, Mg2+, and SO42-. Along the flow direction of groundwater, the hydrochemistry of shallow groundwater show the evolution law from HCO3-Ca·Mg to HCO3·Cl-Na·Ca and HCO3·Cl-Na·Mg, and then to Cl·HCO3-Na·Mg. The hydrochemical types are formed mainly due to the mineral dissolution and deposition, and reaction of cation exchange and adsorption in the aquifer, and the hydrogeochemical processes include leaching, evaporation and concentration, and mixing.

1 Introduction

Shuangliao City is an important part of the Xiliaohe Plain, and one of the most important bases of grain production in the north of China. Groundwater is the main source of water for the residents' life and industrial and agricultural uses. Especially as the Xiliao River has dried up in recent years, Shuangliao developed and utilized groundwater for agricultural uses to a greater extent. The importance of groundwater resources to the region is reflected not only in the water demand, but also the requirement for high quality groundwater. The hydrochemical characteristics and evolution of groundwater have been an important field of research in evaluating the quality of groundwater resources. Related research is of great significance to the utilization and management of groundwater resources and the improvement and protection of ecosystem and environment in the region[1]. The chemical characteristics of groundwater are determined by the sedimentary environment and characteristics of sedimentary combinations of sources, and are affected by natural and human factors such as flood, ecological water transfer, agricultural irrigation[2-5]. Therefore, it is helpful to identify the laws of distribution of groundwater hydrochemical types in understanding the regional hydrogeochemical characteristics, quality and distribution of groundwater in the region, and in guiding the sustainable development and utilization and comprehensive management of groundwater resources in the region[6-8].

By now, Chinese and foreign scholars have carried out a lot of research of hydrochemical characteristics of groundwater, mainly through mathematical statistics[9], Piper or Durov diagrams[10-11], ion proportional coefficient[12], mineral saturation index[13], isotope tracing[14], hydrogeochemical simulation and other techniques to study the chemical characteristics of groundwater and their causes and evolution[15-17]. Generally, many methods are used in related studies, but there is a lack of comprehensive research, especially that of zoning and evolution of regional hydrochemical types. For this reason, after collection of detailed data and identification of the groundwater flow field, we studied the hydrochemical characteristics by zone with mathematical statistics, correlation analysis, ion proportional coefficient and other methods to identify the current hydrochemical characteristics of shallow groundwater in the region, formation of hydrochemical composition and its evolution laws, uncover the main actions forming the hydrochemical composition of groundwater, and provide a scientific basis and management ideas for agricultural production and ecological protection in Shuangliao City and even the whole Xiliaohe Plain.

Author: Li Xuguang, male, born in 1982, master, senior engineer, mainly engaged in research of groundwater pollution, endemic diseases, urban geology, etc. Email: john2011@163.com.
[*] Corresponding author:Zhao Yan, male, born in 1982, master, senior engineer,mainly engaged in research of groundwater pollution, water resources evaluation, etc. Email: 337056992@qq.com.

2 Overview of study area

Shuangliao is a city of Jilin Province located in the transition between semi-humid climate and semi-arid climate, with frequency windy and sandy weather. Its annual average temperature is 6.6 ℃, annual precipitation is 450-550 mm, and annual evaporation is as high as 1,600 mm. Its location is subject to serious land salinization, land desertification and grassland degradation, and is one of the key areas of ecological restoration in Jilin Province.

The aquifers in the study area are mainly of a Quaternary loose rock pore aquifer system, which is composed of three aquifers, namely the Quaternary Holocene, Upper Pleistocene, Middle Pleistocene phreatic aquifers.

(a) Holocene phreatic aquifer: This aquifer is distributed under the floodplains and terraces of the Xinkai River and Xiliao River. It is mainly composed of medium and fine sand with thickness of 10–25 m. The groundwater type is HCO_3-Ca•Na with pH value of 7.34–8.26.

(b) Upper Pleistocene phreatic aquifer: This aquifer is distributed under the low plains and the Songliao watershed. It is composed of sandy loam, silty sand and fine sand with thickness of 3–17m. The type of groundwater is Cl•HCO_3 and SO_4•HCO_3 with pH value of 7.47–8.47.

(c) Middle Pleistocene confined aquifer: This aquifer covers the whole study area, and its lithology is composed of fine sand, silty fine sand and sandy loam with thickness of 5.57–23.5m. The hydrochemical type of groundwater is mainly HCO3 with pH value of 7.37–8.49.

3 Water sample collection and testing

The shallow groundwater samples were collected from June to September 2012. According to the principles of plane control and local densification, the samples were collected with a density of 1.1 group / 100 km^2. 32 groups of shallow groundwater (phreatic water and micro-confined water) samples were collected. Certain protective agents were added and test and analysis were conducted in a timely basis for different test indicators. The samples were tested for 42 indicators, including 7 physical and chemical indicators tested on the field, and 35 inorganic indicators, including "three nitrogen indicators", heavy metals and conventional ions, tested in laboratory.

4 Results and analysis

After the scientific and systematic sampling, testing and analysis of the shallow groundwater across the study area, the methods of descriptive statistics, correlation analysis and ion proportional coefficient in the hydrochemical software (AquaChem4.0) were used to comprehensively and systematically study the hydrochemical characteristics of the shallow groundwater, explore the formation of hydrochemical composition and the evolution laws of regional hydrochemical types, and uncover the main reactions controlling evolution of the groundwater quality and the hydrogeochemical processes.

4.1 Statistical characteristics of hydrochemical parameters

Statistical analysis can reflect the overall picture of groundwater chemical composition in a certain area or a certain period of time[18]. To understand the hydrochemical characteristics of groundwater in this area, the 32 groups of samples collected from June to September 2012 were tested and analyzed, and the statistics of hydrochemical parameters were obtained (Table 1).

Table 1 Statistics of hydrochemical parameters of shallow groundwater

Component	Maximum	Minimum	Average Value	Standard Deviation	Coefficient of variation (%)
Na^+	997.60	10.58	107.65	177.06	164.48
Ca^{2+}	203.50	10.83	78.52	56.60	72.09
Mg^{2+}	176.30	4.31	31.95	32.70	102.34
HCO_3^-	927.86	132.13	347.94	174.97	50.29
Cl^-	1114.39	2.54	102.21	205.14	200.71
SO_4^{2-}	642.37	0.39	89.07	128.68	144.48
NO_3^-	379.63	0.00	50.83	99.48	195.71
TDS	1857.09	184.66	670.27	693.03	103.40
pH	8.3	6.56	7.21	0.35	4.91

Note: In addition to the pH, the units of the concentration of the rest chemical mass parameters are mg/L.

As shown in the above table, that the average concentration of HCO_3^- is the largest, followed by that of Na+ and Cl^-, indicating that these ions are dominant ions in the groundwater. The standard deviations of Cl^-, Na^+ and HCO_3^- are large, indicating that their absolute content in groundwater is high. This is consistent with the larger average concentrations of the three types of irons. The coefficients of variation of Ca^{2+}, Mg^{2+} and HCO_3^- are small, indicating that their content is relatively stable in the groundwater of this region, and the content of HCO_3^- is high and stable. The coefficients of variation of Na^+, Cl- and NO3- are large, indicating that their concentrations vary significantly in different areas and easily affected by the aquifer media, topography, hydrometeorological conditions and human activities. The standard deviation and coefficient of variation of TDS are high, indicating that the content of TDS is high in this region, and the concentrations vary considerably in different areas.

4.2 Correlation characteristics of hydrochemical parameters

Correlation analysis is intended to uncover the similarity and difference in groundwater hydrochemical parameters and the consistency and difference of their sources [1]. With the test results of the 32 groups of groundwater hydrochemistry, statistical software was used to calculate the correlation of typical components (Table 2).

Table 2 Correlation matrices of hydrochemical parameters of shallow groundwater

Component	Na^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	TDS	pH
Na^+	1.000	0.338	0.918	0.774	0.950	0.898	0.350	0.947	0.179
Ca^{2+}		1.000	0.464	0.362	0.505	0.557	0.764	0.603	-0.014
Mg^{2+}			1.000	0.744	0.922	0.903	0.533	0.952	0.160
HCO_3^-				1.000	0.636	0.637	0.179	0.740	0.207
Cl^-					1.000	0.915	0.504	0.968	0.101
SO_4^{2-}						1.000	0.537	0.952	0.204
NO_3^-							1.000	0.594	-0.097
TDS								1.000	0.141
pH									1.000

From the correlation coefficient matrices of hydrochemical parameters, one can see that the correlation coefficients of Cl-, Na+, Mg2+ and SO42- with TDS are high, and the regression equations are shown in formulas (1)–(4).

$$\rho_{TDS}=3.2713\rho Cl^-+335.92 \quad R^2=0.968 \qquad (1)$$

$$\rho_{TDS}=3.7067\rho Na^++271.22 \quad R^2=0.947 \qquad (2)$$

$$\rho_{TDS}=20.175\rho Mg^{2+}+25.652 \quad R^2=0.952 \qquad (3)$$

$$\rho_{TDS}=5.1275\rho SO_4^{2-}+213.57 \quad R^2=0.952 \qquad (4)$$

Where, ρ_{TDS}, ρ_{Cl^-}, ρ_{Na^+}, $\rho_{Mg^{2+}}$ and $\rho_{SO_4^{2-}}$ stand for the concentrations of TDS, Cl^-, Na^+, Mg^{2+} and SO_4^{2-} respectively, in mg/L; R is the correlation coefficient, dimensionless.

From formulas (1)–(4), one can see that the correlation coefficients between TDS and Cl^-, Na^+, $Mg^{2+}$and SO_4^{2-} are above 0.947, while the correlation coefficients between Cl^-, Na^+, Mg^{2+} and SO_4^{2-} in Table 2 are all higher than 0.9. This indicates that the change trend of TDS is consistent with the change trends in concentration of these ions. The correlation coefficients between HCO_3^-, Ca^{2+} and NO_3^-, and the correlation coefficients between them and other ions are poor. Especially, the content of HCO_3^- in groundwater is the highest and stable, and the correlation coefficient between it and TDS is only 0.74, which indicates that the change of TDS in the process of hydrochemical evolution in this region mainly depends on the change of content of Cl-, Na+, Mg^{2+} and SO_4^{2-}. Therefore, it is important to understand the change patterns of these ions for understanding of the evolution process of groundwater in this region.

4.3 Proportion coefficient characteristics of ions

In the chemical composition of groundwater, the content proportional coefficient between various components is often used to study some hydrogeochemical issues[10]. Proportional coefficients can be applied to determine the sources and formation process of groundwater hydrochemical composition. Compared with traditional hydrochemical type analysis along, they enable more deep description and depiction of the evolution process of water quality in spatial dimensions as well as typical analysis of hydrogeochemical evolution.

The γNa/γCl coefficient is called the casual coefficient of groundwater, which is a hydrogeochemical parameter to characterize the enrichment of sodium ions in groundwater. The average value of the γNa/γCl coefficient of standard seawater is 0.85. The γNa/γCl coefficients of low salinity water are high [γNa/γCl > 0.85], while those of high salinity water are low [γNa/γCl<0.85][19]. As shown in Fig. A, almost all the analysis points of water samples are distributed above the straight line 1:1, which indicates that the mg equivalent concentration of [Na^+] is generally greater than that of [Cl^-]. That is, the γNa/γCl coefficient is greater than 1. In the process of runoff, groundwater continuously weathers and dissolves rocks and minerals through hydrolysis and acidification, and Na^+ is thus released from feldspar. As a result, the [Na^+] mg equivalent concentration is greater than that of [Cl^-].

As shown in Fig. B and C, most of the analysis points are located above the straight line 1:1, which indicates that the mg equivalent concentrations of [Ca^{2+}] and [Mg^{2+}] are generally greater than that of [SO42-] concentration, and the mg equivalent concentration of [Ca^{2+}] is higher than that of [Mg^{2+}]. Along the flow direction of groundwater, TDS gradually increases, which facilitates the dissolution of calcite and dolomite. In Fig. D, most of the analysis points are located above the straight line 1:1, which indicates that the dissolved amount of calcite is higher than that of dolomite. Fig. E shows that the analysis points are below the straight line 1:1, which indicates that the mg equivalent concentrations of [Ca^{2+}+Mg^{2+}] are lower than that of [HCO_3^-+SO_4^{2-}]. This suggests the weathering-dissolution of carbonate rocks occurring in the process of transport by groundwater.

Cl^-, SO_4^{2-} and HCO_3^- characterize the dissolution of rock salt, gypsum and dolomite respectively, so $\gamma(Na^+-Cl^-)$ and $\gamma(HCO_3^-+SO_4^{2-}-Ca^{2+}-Mg^{2+})$ represent the dissolution of the three minerals. If there is cation exchange and adsorption, the ratio of $\gamma(Na^+-Cl^-)$ to $\gamma(HCO_3^-+SO_4^{2-}-Ca^{2+}-Mg^{2+})$ should be close to 1[20]. Most analysis points in Fig.

F are located near the straight line 1:1, this indicates that cation exchange and adsorption occurs in the process of transport by groundwater.

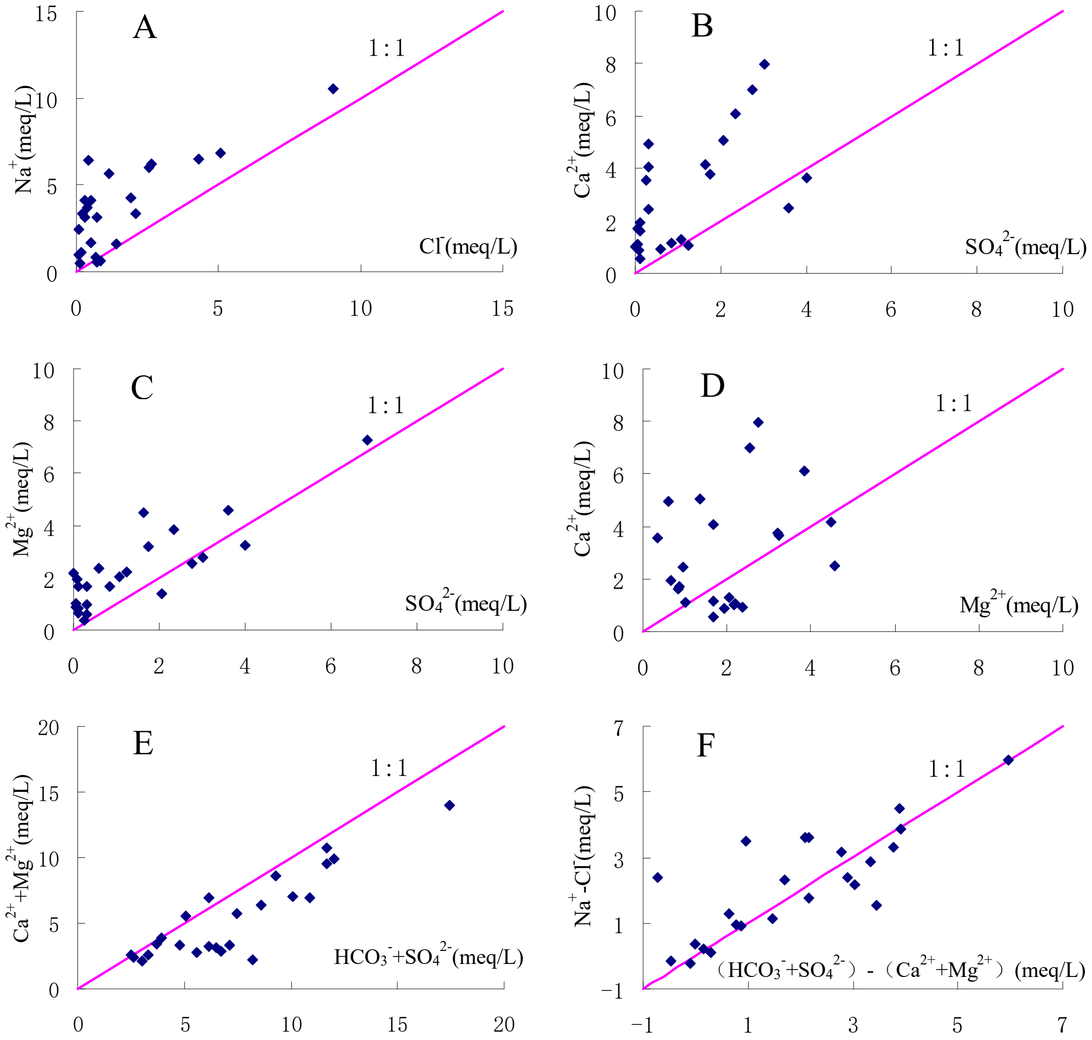

Fig. 1 Hydrochemical relationships between the selected ions of shallow groundwater

As shown in the left diagram of Fig. 2, when TDS<500mg/L, the γNa/γCl coefficient trends to increase along with the increase of TDS. This indicates that in low salinity water bodies, with the increase of groundwater flowing distance, the concentration of Na^+ from mineral weathering and dissolution gradually increases, resulting in the increase of Na^+ content in groundwater, and gradually increases downstream. When TDS>500mg/L, the γNa/γCl coefficient generally increases with the increase of TDS. This indicates that when TDS in groundwater reaches a certain concentration, Na+ starts iron exchange with Ca2+ and Mg2+ adsorbed by clay minerals in aquifers, resulting in the decrease of Na+ concentration and increase of Cl^- in groundwater, so the γNa/γ coefficient decreases.

As shown in the right diagram of Fig. 2, when TDS<500mg/L, the ratio of $\gamma(Na\text{-}Cl)/\gamma(Ca+Mg\text{-}HCO_3\text{-}SO_4)$ changes remarkably, and only a few points have ratio values close to 1. When TDS>500mg/L, the ratio of $\gamma(Na\text{-}Cl)/\gamma(Ca+Mg\text{-}HCO_3\text{-}SO_4)$ falls on a straight line, which indicates that cation exchange and adsorption occurs. In this case, the concentration of Na^+ ions decreases and the concentrations of Ca^{2+} and Mg^{2+} increase, which is consistent with the change law of the γNa/γCl coefficient along with TDS.

With the increase of TDS concentration, not only the dissolution and precipitation of rock salt, gypsum and dolomite, but also cation exchange and adsorption occur between groundwater and aquifer media. Therefore, the dissolution and precipitation of minerals and the cation exchange and adsorption are of great significance to the formation of groundwater hydrochemical characteristics.

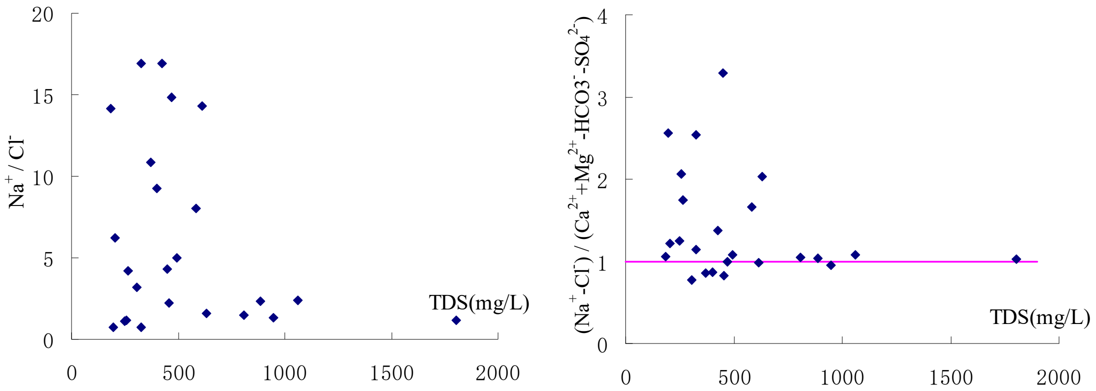

Fig. 2 Chart of γNa/γCl, γ(Na-Cl)/γ(Ca+Mg-HCO_3-SO_4) with the changing concentration of TDS

4.4 Regional characteristics of groundwater hydrochemical evolution

From the analysis above, we know the hydrochemical characteristics of shallow groundwater and explore its causes, but its spatial distribution and evolution laws are not presented in a sufficiently intuitive manner. Therefore, according to the results of test data with water samples, we applied the Sukharev classification method to classify the hydrochemical types of shallow groundwater, and the results of classification are shown in Fig. 3.

As shown in Fig. 3, shallow groundwater flows from northeast to southwest. By comparing the test results of TDS against the direction of groundwater flow, the concentration of TDS is found to gradually increases from northeast to southwest. Generally, the concentration of TDS is less than 500 mg/L in the northeast, 500–1000 mg/L in the middle and higher than 1,000 mg/L in southwest. In the northeast of the region, the runoff conditions of groundwater is favorable, and the water exchange is relatively rapid. The soluble components Cl$^-$, Na+ and SO_4^{2-} in the aquifer are continuously leached and transported with the water flow. The ions are mainly Ca^{2+} and HCO_3^-, forming low salinity HCO_3-Ca·Mg water. This is consistent with the conclusion in 3.3 that when TDS < 500mg/L, the concentration of Na^+ in the groundwater flowing downstream increases due to weathering and dissolution of minerals . The groundwater flow slows down in the middle of the region. With the increase of groundwater flowing distance and residence time, there is sufficient time of reaction for the dissolution of calcite, dolomite and other minerals, which makes the concentration of Ca^{2+} and Mg^{2+} ions in groundwater increase. Since the TDS this area is 500–1,000, it is possible to infer from 3.3 that cation exchange and adsorption occurs in slow runoff area, which further increases the content of Ca^{2+} and Mg^{2+} ions in the groundwater, and forms medium salinity HCO_3·Cl-Na·Ca and HCO_3·Cl-Na·Mg water. In the southwest of the region, TDS is higher than 1,000 mg/L, in which case Ca^{2+} and Mg^{2+} ions are easy to form carbonate precipitation. Moreover, the amount of calcite precipitation is higher than that of dolomite, resulting in decrease of concentrations of Ca^{2+}, Mg^{2+} and HCO_3^- ions in the groundwater, forming high salinity Cl·HCO_3^-Na·Mg water.

Along the flow direction of groundwater, the hydrochemistry of shallow groundwater show the evolution law from HCO_3-Ca·Mg to HCO_3·Cl-Na·Ca and HCO_3·Cl-Na·Mg, and then to Cl·HCO_3-Na·Mg. The hydrochemical types are formed mainly due to the mineral dissolution and deposition, and reaction of cation exchange and adsorption in the aquifer, and the hydrogeochemical processes include leaching, evaporation and concentration, and mixing.

5 Conclusions

(1) The concentrations of HCO3-, Cl- and Na+ in the shallow groundwater of Shuangliao City are relatively high, while the concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-} and NO_3^- - are relatively low. The concentration of TDS increases gradually along the flow direction of groundwater, and TDS is positively correlated to the variation in concentration of Cl-, Na+, Mg2+ and SO_4^2-.

(2) Along the flow direction of groundwater, the hydrochemistry of shallow groundwater show the evolution law from HCO3-Ca·Mg to HCO3·Cl-Na·Ca and HCO3·Cl-Na·Mg, and then to Cl·HCO3-Na·Mg.

(3) The hydrochemical types are formed mainly due to the mineral dissolution and deposition, and reaction of cation exchange and adsorption in the aquifer, and the hydrogeochemical processes include leaching, evaporation and concentration, and mixing.

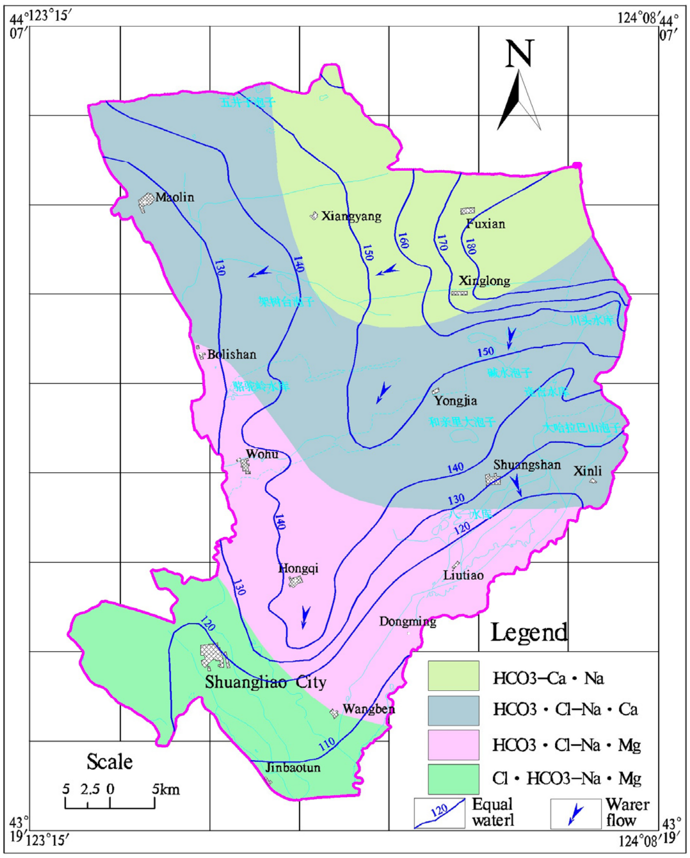

Fig. 3 Hydrochemical type diagram in shallow groundwater

References

1. Zhang, G, Deng, W, He, Yan, et al. （2006）Hydrochemical characteristics and evolution laws of groundwater in Songnen Plain, Northeast China . Advances In Water Science, 17(1) : 20-28.
2. Xie, Z, Liu, K, Li, Z, et al. (2010)Analysis of groundwater chemical characteristics based on sediment provenance analysis: A case study of Beijing Plain . Earth Science Frontiers, 17(6):81-87.
3. Xu, H, Zhao, T, Meng, H, et al. (2011)Relationship between groundwater quality index of physics and chemistry in riparian zone and water quality in river . Environment Science, 32(3) :632-640.
4. Chen, Y, Chen, Y, Li, W, et al. (2006)Three stages of the groundwater chemical properties reacting on the intermittent water deliveries in lower Tarim River, China. Environment Science, 27(7):1299-1304.
5. Ma F, Yang Y S, Yuan R, et al. (2007)Study of shallow groundwater quality evolution under saline intrusion with environmental isotopes and geochemistry. Environmental Geology, ,51(6): 1009-1017.
6. Ding, H, Zhang, J. (2005)Goechemical properties and evolution of groundwater beneath the Hexi corridor, Gansu province. Arid Zone Research, 22(1):24-28.
7. Liao, Z, Lin, X. (2004)Chemical characteristics and variations of groundwater quality in Songnen Basin . Journal of China University of Geosciences, 29(1): 96-102.
8. Li, C, Gao, X, Wang, Y. (2015)Hydrogeochemistry of high-fluoride groundwater at Yuncheng Basin, northern China. Science of the Total Environment, (508): 155-65.
9. Pu, T, He, Y, Zhang, T, et al. (2013)Isotopic and geochemical evolution of ground and river waters in a karst dominated geological setting: A case study from Lijiang basin, South-Asia monsoon region. Applied Geochemistry, 6(33): 199-12.
10. Martin B Goldhabera, Christopher T Millsb, Jean M Morrisonb, et al. (2014)Hydrogeochemistry of prairie pothole region wetlands: Role of long-term critical zone processes. Chemical Geology, 10(387): 170-83.
11. Han, D, Song, X, Matthew J Currell, et al. (2011)A survey of groundwater levels and hydrogeochemistry in irrigated fields in the Karamay Agricultural Development Area, northwest China: Implications for soil and groundwater salinity resulting from surface water transfer for irrigation . Journal of

Hydrology, 8(405):217-234.

12. Charles N Alpers, Donald O Whittemore. (1990)Hydrogeochemistry and stable isotopes of ground and surface waters from two adjacent closed basins, Atacama Desert, northern Chile. Applied Geochemistry, 10 (5):719-734.
13. Guo, Q. (2012)Hydrogeochemistry of high-temperature geothermal systems in China: A review . Applied Geochemistry, 10(27):1887-1898.
14. Maurizio Barbieri , Marco Morotti. (2003)Hydrogeochemistry and strontium isotopes of spring and mineral waters from Monte Vulture volcano, Italy. Applied Geochemistry, 1 (18):117-125.
15. Su, Y, Feng Q, Zhu G, et al. (2007)Identification and evolution of groundwater chemistry in the Ejin Sub-Basin of the Heihe River, northwest China [J]. Pedosphere, 17(3) : 331-342.
16. Belkhiri L, Boudoukha A, Mouni L, et al. (2010)Application of multivariate statistical methods and inverse geochemical modeling for characterization of groundwater-A case study: Ain Azel plain (Algeria). Geoderma, 159(3-4): 390-398.
17. Bennetts D A, Webb J A, Stone D J M, et al. (2006)Understanding the salinisation process for groundwater in an area of south-eastern Australia, using hydrochemical and isotopic evidence [J]. Journal of Hydrology, 323(1-4): 178-192.
18. Jiang, L. (2009)Study on the formation and evolution mechanism of groundwater chemical composition in arid oases -- a case study of Yaoba Oasis in Alashan Chang'an: Chang'an University.
19. Yang, T, Wang, M, Chen, L. (1998)Hydrogeochemical characteristics and causal analysis of Dongying Basin. Proceedings of the 30th International Geological Congress Vol. 22. Beijing: Geological Publishing House.
20. An, L, Zhao, Q, Ye, S, et al. (2012)Hydrochemical characteristics and formation mechanism of shallow groundwater in the Yellow River Delta. Environment Science, 33(2):370-378.