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Hydrochemical characteristics and evolution laws of shallow groundwater in Shuangliao city

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ABSTRACT

Shuangliao city is an important part of Weat Liaohe river plain, to ascertain hydrochemical characteristics, origin and evolution of groundwater will be the guiding role to develop and ecological construct to the West Liaohe Plain. In the basis of groundwater flow field, combination of mathematical statistics, correlation analysis, ion scale factor and other methods, hydrochemical characteristics of groundwater will be researched by partition. The result shows that the concentrations of HCO_3^-,Cl^-,Na^+ are higher, and these of Ca^{2+},Mg^{2+},SO_4^{2-},NO_3^- are lower. The concentration of TDS increase gradually in the flow, variation of the concentration of TDS, Cl^-,Na^+, Mg^{2+},SO_4^{2-} is correlated. Hydrochemical characteristics and evolution laws of shallow groundwater is from HCO3-Ca•Mg to HCO3•Cl-Na•Ca, HCO3•Cl-Na•Mg, and then to Cl•HCO3-Na•Mg. The formation of hydrochemical type was mainly due to the reaction of mineral dissolution, cation exchange and adsorption in the aquifer, hydrogeochemical processes is leaching, evaporation, mixing.

Keywords: shallow groundwater, hydrochemical characteristics, evolution laws, Shuangliao city.

INTRODUCTION

Hydrochemical characteristics and evolution laws of groundwater are an important research content in assessment of groundwater quality, the relevant research is of great significance to the use and management of groundwater resources and the construction and protection of ecological environment [1]. Hydrochemical characteristics of groundwater are determined by the sedimentary depositional environment of provenance, and are influenced by floods, ecological water, agricultural irrigation and other natural and human factors [2-5]. Therefore, to identify the distribution hydrochemical type is benefit to understand the hydrochemical characteristics, groundwater quality, it will be the guiding role to sustainable development and utilization of regional groundwater resources and integrated management.

At present, domestic and foreign scholars have done so much research about hydrochemical characteristics of groundwater for groundwater chemical characteristics, hydrochemical characteristics of groundwater, and their causes, evolution are researched by Mathematical Statistics, Piper or Durov diagram, the ion ratio coefficient, mineral saturation index, isotope tracer techniques and hydrogeochemical modeling methods [6-9]. That can be concluded more methods, but less comprehensive study, and much fewer regional hydrochemical type. So, in the based of determining groundwater flow field, combining the methods of Mathematical statistics, correlation analysis, ion ratio coefficient, hydrochemical characteristics of groundwater will be researched by partition. It is seek to clarify the main formation of chemical compositions, in order to provide scientific management ideas during the development, construction and ecological protection of the West Liaohe River Plain.

Study area

Shuangliao City, Jilin Province is located in semi-humid and semi-arid climatic zones to the transition zone, with more sand characteristics. The annual average temperature is 6.6℃, the annual precipitation is 450-550mm, but the annual evaporation is as high as 1600mm. Land salinization, land of sand and grassland degradation are very serious, so, it is one of the key areas of ecological construction in Jilin Province.

The study area is mainly Quaternary loose rock pore aquifer system, it consists of three components, namely Quaternary Holocene, Pleistocene, and Middle Pleistocene unconfined aquifer.

(a) Holocene unconfined aquifer: The aquifer distribute in Xinkai River and floodplain and terraces of the West Liaohe River, it is consist of medium sand and fine sand, its thickness is 10-25m. Hydrochemical type is HCO3-Ca • Na, pH is 7.34-8.26.

(b) Upper Pleistocene unconfined aquifer: The aquifer locates in the watershed of Songliao Plain, it is consist of sandy loam, silt and sand, its thickness is 3-17m. Hydrochemical type is Cl • HCO3, SO4 • HCO3, pH is 7.47-8.47.

(c) Middle Pleistocene confined aquifer: The aquifer is throughout the region, the lithology is about sand, fine sand and sandy loam, its thickness is 5.57-23.5m. Hydrochemical type is mainly HCO3, pH is 7.37-8.49.

Water sampling and testing

The sampling time was from June to September in 2012, water sampling is followed the principle of control and local refinement, sampling density is 1.1 Groups/100km^2. Collection of Shallow groundwater samples were collected to 32 groups. The total test indicators were 42, including 7 physical and chemical testing indicators in the field, 35 laboratory testing inorganic indicators, such as "Three Nitrogen" , total hardness , TDS , etc.

RESULTS AND DISCUSSION

Based on the scientific and systematic sampling and testing, using Hydrological Chemical Software (AquaChem4.0), the integrated analysis methods is about descriptive statistics, correlation analysis, ion scale factor and other methods, hydrochemical characteristics of groundwater will be researched by partition. It is seek to clarify the main formation of chemical compositions, in order to reveal the hydrogeochemical and main reaction process in the evolution of groundwater quality.

Statistical characteristics of chemistry parameters

Statistical analysis may roughly reflect chemical constituents of groundwater in a particular region or period of time [10]. Therefore, in order to understand hydrochemical characteristics, the testing data is statistical analysis; the statistical characteristics related to water chemistry parameters values shows in Table 1.

Table 1 Statistics of hydrochemical parameters of shallow groundwater

Components	Maximum	Minimum	Average	Standard Deviation	Variable Coefficient %
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

Note: In addition to pH, the rest of the concentrations of hydro-chemical parameters are mg/L

The table shows that average concentration maximum is HCO_3^-, and Na^+, Cl^- followed, it means that these are dominate in groundwater ions. The standard deviation of HCO_3^-, Na^+, Cl^- is larger, demonstrating its high absolute, which is the same as the larger concentration. Variable coefficients of Ca^{2+}, Mg^{2+}, HCO_3^- are smaller, indicating that the content is relatively stable in the groundwater, but these of Na^+, Cl^-, NO_3^- are larger, indicating which differ in different regions, so, it is vulnerable influenced by aquifer media, topography, hydrological and meteorological conditions and human activities and other factors. The standard deviation and variable coefficient of TDS are higher, showing the higher concentrations and different of TDS in the region.

Correlation characteristics of chemistry parameters

Correlation analysis can reveal the similarity and consistency of chemical parameters and sources of dissimilarity and differences [1]. According to testing results of samples, the correlation of typical components is calculated by statistical software, showing in Table 2.

Table 2 Correlation matrices of hydrochemical parameters of shallow groundwater

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

The correlation matrix means that Na^+, Cl^-, Mg^{2+}, SO_4^{2-} and TDS are higher correlation coefficient; it can be expressed by the regression equation (1) to (4).

$$\rho_{TDS} = 3.2713\rho_{Cl^-} + 335.92 \qquad R^2 = 0.968 \tag{1}$$
$$\rho_{TDS} = 3.7067\rho_{Na^+} + 271.22 \qquad R^2 = 0.947 \tag{2}$$
$$\rho_{TDS} = 20.175\rho_{Mg^{2+}} + 25.652 \qquad R^2 = 0.952 \tag{3}$$
$$\rho_{TDS} = 5.1275\rho_{SO4^{2-}} + 213.57 \qquad R^2 = 0.952 \tag{4}$$

Where ρ_{TDS}, ρ_{Cl^-}, ρ_{Na^+}, $\rho_{Mg^{2+}}$, $\rho_{SO4^{2-}}$ are the concentration of TDS, Cl^-, Na^+, Mg^{2+}, SO_4^{2-} respectively, with units of mg/L; R is the correlation coefficient, dimensionless.

Equation (1) - (4) shows that the correlation of TDS and Na^+, Cl^-, Mg^{2+}, SO_4^{2-} is more than 0.947, correlations in the between of Na^+, Cl^-, Mg^{2+}, SO_4^{2-} are all higher than 0.9 shown in Table 2, the trend of changing concentrations between TDS and of the other ions is consistent. It indicating that the changing concentration of TDS is determined by Na^+, Cl^-, Mg^{2+}, SO_4^{2-} in the process of hydrochemical evolution, so, it is necessary and for understanding the variation of these ions for to determine the evolution of the regional hydrochemical characteristics.

Ratio characteristics of ions coefficient

The ratio coefficients of chemical composition are often used to study some of the hydrogeochemical problems [10]. It can be used to determine the source and formation process of groundwater chemical composition, it is more in-depth than traditional hydrochemical analysis to describe and depict the evolution of spatial scales.

The coefficient of γ_{Na}/γ_{Cl} called causes factor of groundwater, it is a hydrogeochemical parameter to characterize the degree of concentration of sodium ions. γ_{Na}/γ_{Cl} of standard seawater average is 0.85, the lower salinity, the higher γ_{Na}/γ_{Cl} [γ_{Na}/γ_{Cl} > 0.85], otherwise higher [γ_{Na}/γ_{Cl} <0.85] [11]. It can be seen substantially analysis points located above the straight line 1:1 in Figure A, indicating coefficient of γ_{Na}/γ_{Cl} is greater than 1, rock and mineral was weathered and dissolved continuously by hydrolysis and acidification during groundwater runoff process, Na^+ released from feldspar , so that [Na^+] is greater than the milliequivalent concentration of Cl^-.

Figure B, C, D shows that the majority of points are above the straight line 1:1, indicating that the milliequivalent concentration is [Ca^{2+}] > [Mg^{2+}] > [SO_4^{2-}]. Along the flow, TDS gradually increased, while the elevated TDS will promote calcite, dolomite dissolution, so, the dissolution amount of calcite is higher than dolomite. Figure E means the milliequivalent concentration of [Ca^{2+}+Mg^{2+}] is below [HCO_3^-+SO_4^{2-}], illustrating carbonate weathering-dissolution was occurred in the process of groundwater migration.

The dissolution of halite, gypsum and dolomite is characterized by Cl^-, SO_4^{2-}, HCO_3^-, respectively, therefore, $\gamma(Na^+-Cl^-)$ and $\gamma(HCO_3^-+SO_4^{2-}-Ca^{2+}-Mg^{2+})$ can represent the three minerals dissolved. If there is cation exchange and adsorption, the ratio of $\gamma(Na^+-Cl^-)$ and $\gamma(HCO_3^-+SO_4^{2-}-Ca^{2+}-Mg^{2+})$is close to one [12]. Most of the analysis points in Figure F is up and down about the straight line 1:1, description cation exchange and adsorption occurred during groundwater migration.

Figure 2 shows that when TDS<500mg/L, γ_{Na}/γ_{Cl} upward trend with TDS increases, it means that the concentration of Na^+ gradually increased from mineral weathering-dissolved with groundwater flow in low salinity; if TDS>500mg/L, γ_{Na}/γ_{Cl} downward trend with TDS increases, [Na^+] exchanges [Ca^{2+}], [Mg^{2+}] adsorbed in clay minerals, resulting in the concentration of Na^+ decreases, contrary Cl^- increases, so, coefficient of γ_{Na}/γ_{Cl} decreased.

It can be seen in Figure 2 that when TDS<500 mg/L, the ratios of $\gamma_{(Na-Cl)}/\gamma_{(Ca+Mg-HCO3-SO4)}$ are variations, only individual points are close to 1; when TDS>500mg/L, the ratio falls to straight line, indicating cation exchange and adsorption occurs, this conclusion is consistent to laws of γ_{Na}/γ_{Cl} with the variation concentrations of TDS.

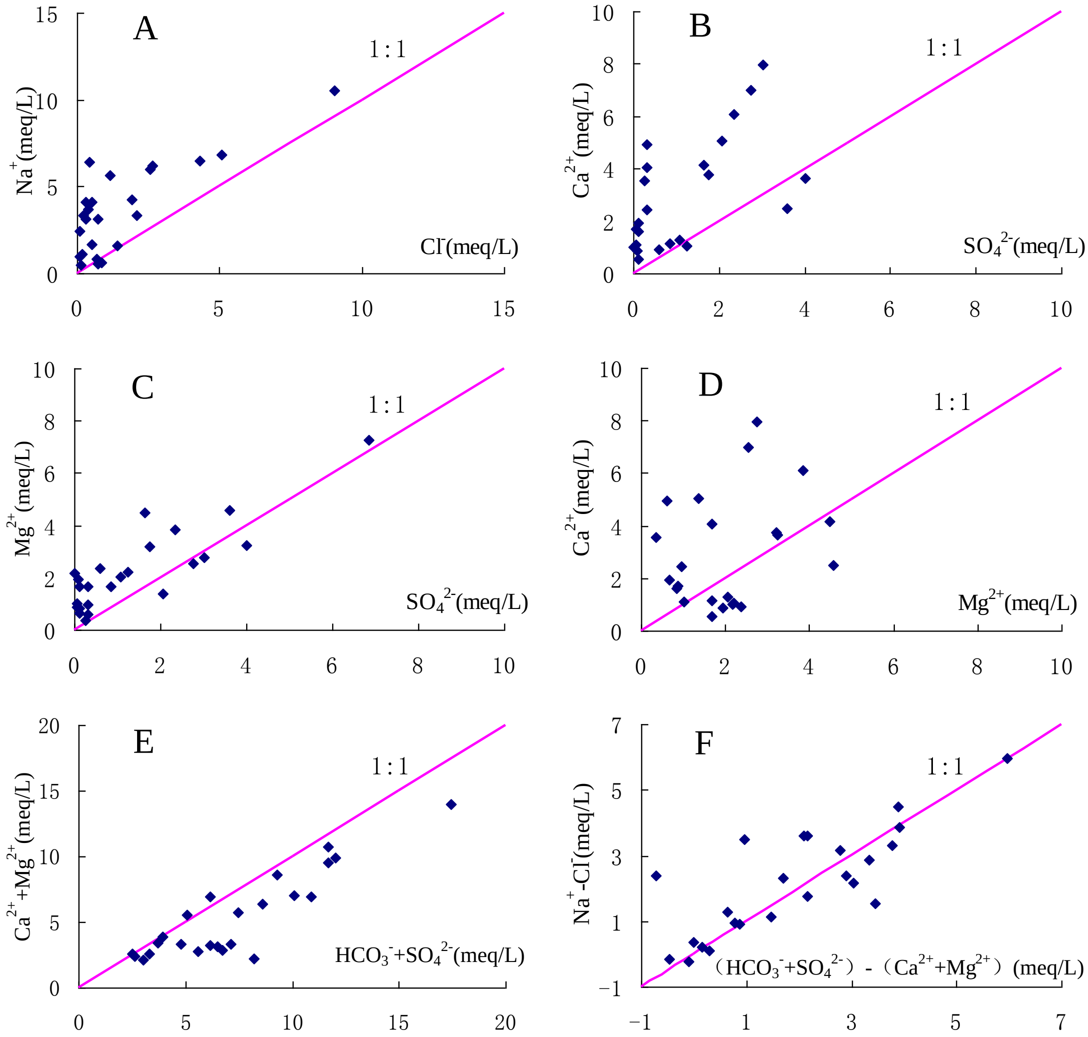

Fig. 1 Hydrochemical relationships between the selected ions of shallow groundwater

With the variation concentrations of TDS, dissolution and precipitation of halite , gypsum and dolomite, and cation exchange and adsorption occurs between groundwater and the media halite, therefore, dissolution, precipitation and cation exchange and adsorption are of great significance for the formation of hydrochemical characteristics.

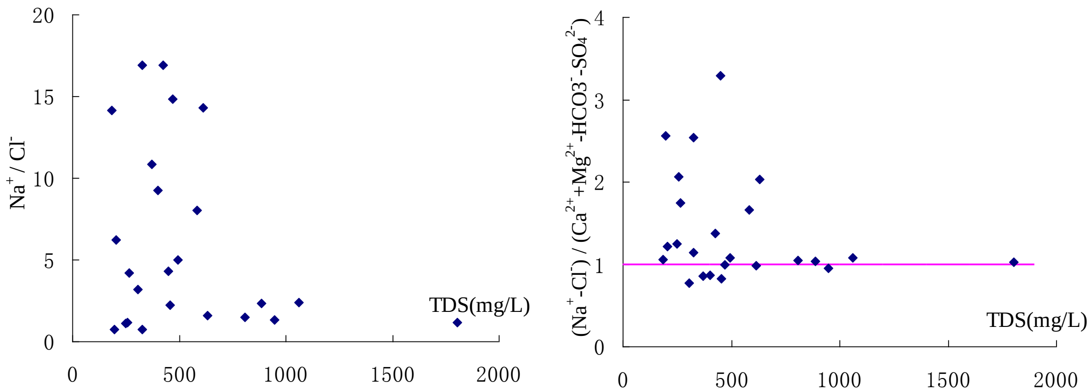

Fig. 2 The chart of γ_{Na}/γ_{Cl}, $\gamma_{(Na-Cl)}/\gamma_{(Ca+Mg-HCO3-SO4)}$ with the changing concentration of TDS

Regional hydrochemical evolution

The above analysis shows that shallow hydrochemical characteristics and causes of groundwater, but its spatial distribution and evolution are not intuitive. Therefore, using Shukaliefu classification to determine hydrochemical type, and showing in Figure 3.

The flow of shallow groundwater is from northeast to southwest, according to test results of TDS comparing groundwater flow, concentration of TDS increased gradually from northeast to southwest, and the concentration of TDS in the Northeast is generally less than 500mg/L, Central is typically 500-1000 mg/L, Southwestern is more than 1000 mg/L. Groundwater flow condition in the Northeas was better, the soluble components of Cl^-, Na^+, SO_4^{2-} were leached continually in the flow, , ions were mainly Ca^{2+}, HCO_3^-, the formation of hydrochemical type in low salinity is HCO3-Ca•Mg, which is consistent with the conclusion in Section 3.3.Regional central groundwater flow slowed down, with the growth of residence time of flow,it can provide adequate response time to calcite, dolomite and other minerals dissolved, making the concentration of Ca^{2+}, Mg^{2+} increase, from Section 3.3, we could know that cation exchange and adsorption occurred between Ca^{2+}, Mg^{2+} and Na^+, thus further making the concentration of Ca^{2+}, Mg^{2+} increase, the formation of hydrochemical type in moderate salinity is HCO3•Cl-Na•Ca, HCO3•Cl -Na•Mg. The concentration of TDS in southwestern region is higher than 1000 mg/L, Ca^{2+}, Mg^{2+} are easy to be generated carbonate precipitation, calcite precipitation was higher than dolomite, resulting the concentration of Ca^{2+}, Mg^{2+}, HCO_3^- decrease, the formation of hydrochemical type in high salinity is Cl•HCO3-Na•Mg.

Along the flow direction of groundwater, hydrochemical type evolution of shallow groundwater is from HCO3-Ca•Mg with low salinity, to HCO3•Cl-Na•Ca, HCO3•Cl-Na•Mg with moderate salinity, then to Cl•HCO3-Na•Mg with high salinity. The formation of hydrochemical type was mainly due to the reaction of mineral dissolution, cation exchange and adsorption in the aquifer, hydrogeochemical processes is leaching, evaporation, mixing.

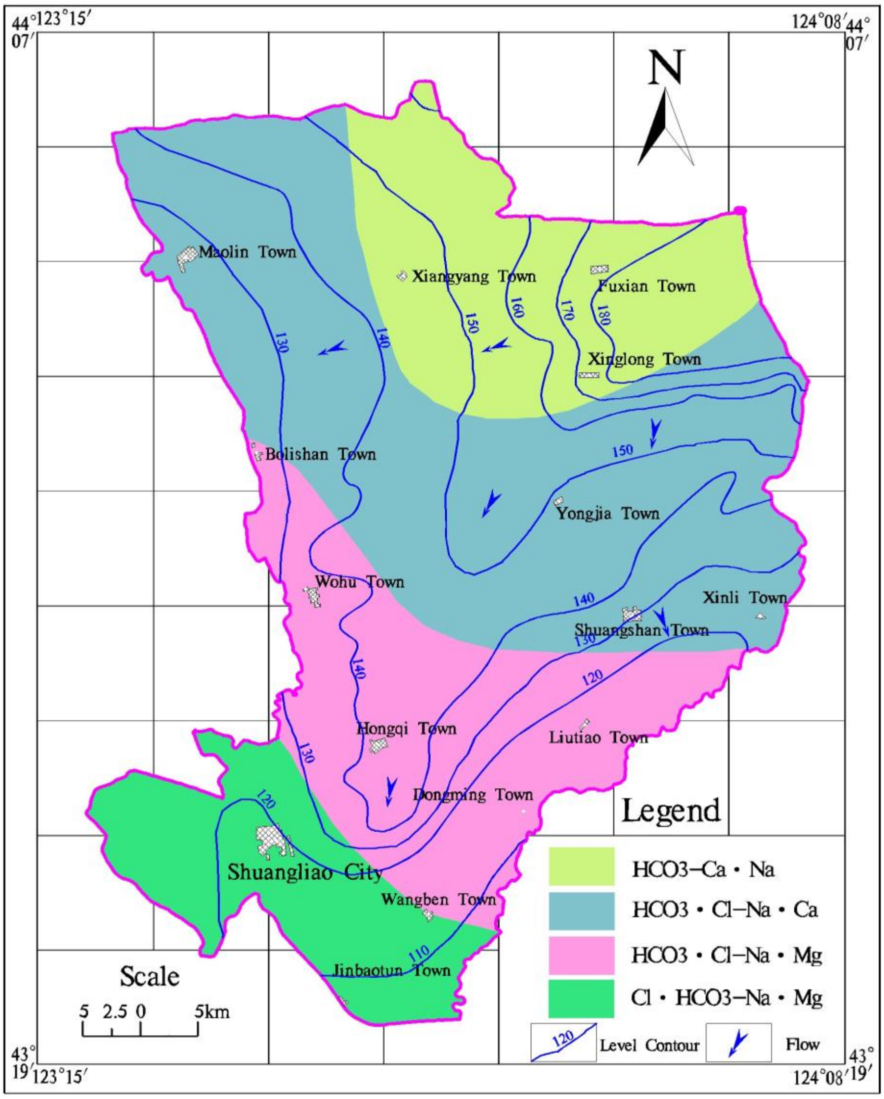

Fig. 3 Hydrochemical type diagram in shallow groundwater

CONCLUSION

(1) The concentrations of HCO_3^-, Cl^-, Na^+ are higher, and these of Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^- are lower. The concentration of TDS increase gradually in the flow, variation of the concentration of TDS, Cl^-, Na^+, Mg^{2+}, SO_4^{2-} is correlated.

(2) Hydrochemical characteristics and evolution laws of shallow groundwater is from HCO3-Ca•Mg to HCO3•Cl-Na Ca, HCO3•Cl-Na Mg, and then to Cl•HCO3-Na•Mg.

(3) The formation of hydrochemical type was mainly due to the reaction of mineral dissolution, cation exchange and adsorption in the aquifer, hydrogeochemical processes is leaching, evaporation, mixing.

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