Hydrochemistry and Stable Isotope Indication of Mineral Water and Surface Water in Changbai Mountain, China

Running title: Study on mineral water in Changbai Mountain, China

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Abstract

Changbai Mountain is the source region of Songhua River, Tumen River and Yalu River. It is a famous concentrated distribution area of high quality mineral water in China, which has great economic value. Antu County is one of the main distribution areas of basalt and mineral water in Changbai Mountain. The distribution of mineral springs has a strong hydraulic relationship with surface water, which constitutes abundant recharge reserves. It is necessary to study the hydrochemical characteristics and relationship between surface water and mineral water, so as to provide a theoretical basis for further discussion on the formation process and rational utilization of mineral water resources in Changbai Mountain. 57 water samples from 2016 to 2020 were collected, including precipitation, mineral water and surface water. Geostatistics, Piper and Gibbs diagram are used to analyze the hydrochemical characteristics. Hydrochemical component tracing and stable environment isotope technology with end-number calculation are used to reveal the transformation relationship between mineral water and surface water. Results demonstrate: Surface water and mineral water are weak alkaline and low salinity. The hydrochemical type of mineral water is mainly HCO_3-Na·Mg·Ca and of surface water is mainly HCO_3-Na. The isotopes of precipitation are more enriched in summer due to the influence of water vapor source and temperature effect. The temporal and spatial differences between D and ^{18}O of mineral water is obvious, and isotopes are enriched abundant in autumn. The recharge source and interaction between mineral water and surface water have changes in different periods. In summer, mineral springs in Erdaobai River and Sandaobai River watershed replenished surface water, and the recharge proportion is more than 60%. The interaction between Toudao Baihe river and mineral water is weak. In autumn, precipitation is the main recharge for mineral water and surface water.

Key words: mineral water; surface water; stable isotopes; hydrochemistry; Changbai Mountain

1. INTRODUCTION

Surface water and groundwater transformation is an important part of watershed water cycle, and is also the basic research of river maintenance mechanism, groundwater regeneration rate and ability(Sophocleous, 2002). Groundwater and surface water resources and the process of hydrochemical formation and evolution are closely related to the interaction between them(Chapman et al., 2007; Intaraprasong & Zhan, 2009). As one of the main groundwater forms in Changbai Mountain area, mineral water has a significant influence on the water resources in the watershed. The basalt area of Changbai Mountain is the third largest existing source of high-quality natural mineral water in the world after the Caucasus Mountain and the Alps. Mineral spring resources are mainly distributed in Jingyu, Fusong and Antu county(Song, 1984). Along with the social and economic development, people's healthy awareness of drinking water is increasing, which makes the demand for high quality mineral water increase. Antu County is one of the main distribution areas of basalt and mineral water in Changbai Mountain. Its mineral water types are diverse, with abundant reserves. So there is great development potential and economic value. The water system in this region is developed and the river network is interlaced. The distribution of mineral springs has a strong hydraulic relationship with surface water, which constitutes abundant recharge reserves. With the deepening development and utilization of mineral water resource formation mechanism in Changbai Mountain ，the mineral water replenishment’s changes and quality’s sustainability in different periods, seasons and utilization stages should be further ascertained. Studying the relationship between mineral water and surface water in this area will provide a new way for the research on the formation of mineral water and theoretical basis for the sustainable development and utilization of mineral water resources in Changbai Mountain.

Various studies of mineral water in Changbai Mountain have been conducted. Some researchers summarized the characteristics and distribution regularity of natural mineral water resources in Changbai Mountain area(Wang & Zhang, 2019; Zhao et al., 2005), and analyzed the significance of mineral water to human health(Liu & Zhang, 2009; Yin et al., 2008). According to the existing data, there were comprehensive analysis of the geological background and distribution characteristics of Jingyu mineral water field(Duan & Qi, 2014; Zhang, 2001). And basing on experiments, Xiao, Yuan, Liang, Yang, & Sun (2019) and Yan, Xiao, Liang, & Wu (2017)explored the formation process of the characteristic component H_3SiO_3 in Jingyu basalt mineral water. By combining experiments and simulations, the recharge conditions and sources of mineral water and formation mechanism of mineral springs in Fusong and Jingyu area were respectively studied(Gao et al., 2016; Liang et al., 2019; Yan et al., 2016; Zhang et al., 2020; Zhang et al., 2017). Bian et al. (2019) studied the carrying capacity of Fusong mineral water resources. In a whole, these researches mainly focus on the evaluation and utilization and formation mechanism of mineral water resources in the basalt area of Jingyu and Fusong area, with emphasis on the influence of geological conditions and water-rock interaction. However, the research on the relationship between mineral water and surface water in Antu area is still insufficient.

Chemical components in groundwater and surface water are related to recharge, runoff and discharge and occurrence conditions. Solutes in water exchange synchronously with the change of water quantity. And chemical composition of natural water records the history of water formation and transport to a certain extent(Vaughn & Fountain, 2005). The migration of hydrochemical components of surface water and groundwater along the flow direction can reflect the different degrees of hydrochemical reactions in water with the change of distance. And by analyzing the change of hydrochemical components, the transformation relationship between surface water and groundwater can be qualitatively determined and the cyclic evolution characteristics of groundwater and surface water can be revealed. The environmental isotopes in groundwater are stable, so they play a tracer role in groundwater circulation. Changes in the concentration of stable isotopes (D and ^{18}O) in different water bodies can trace their formation and migration patterns, and reveal the law of water circulation and mutual transformation process of different water bodies under the changing environment(Song et al., 2002; Unnikrishna et al., 2002). Usually, the mixing of isotopes is an important reason for the change of isotopes in water bodies. The common mixing of atmospheric precipitation and other types of water is a binary mixture(Gu, 2011). According to the stability of hydrogen and oxygen environment isotopes, the conversion relationship between different water bodies can be described quantitatively.

Since the 1950s, environmental isotope technology has developed rapidly and been widely used in the study of water recharge sources and interrelationships. By using the environmental isotope technology to analyze the changes of stable isotopes, the recharge source and range of different water bodies can be obtained(Guo et al., 2015; Liu & Yamanaka, 2012; Mohammed et al., 2012; Payne et al., 1978; Strauch et al., 2006; Vaughn & Fountain, 2005; Zhong et al., 2019). Katz, Coplen, Bullen, & Davis (2010)proposed a quantitative research method for surface water and groundwater system by using the isotopes and water chemical composition characteristics of groundwater and surface water. In addition, a lot of studies have shown that combining hydrochemical and isotopic characteristics in different water bodies can reveal the transformation relations among them(Katz et al., 2010; Musgrove et al., 2010; Rautio & Korkka-Niemi, 2015; Song et al., 2006; Sophocleous, 2002; Zhang et al., 2016).

On the base of the hydrochemistry and stable isotope data of mineral water and surface water from data collection and field sampling, this paper analyzes hydrochemistry type and the source of main chemical components. By comparing hydrochemistry and isotope distribution characteristics, we describe the influencing factors of them and reveal the mutual transformation relationship between mineral water and surface water, which will provide a reference for protection and rational utilization of mineral water resources in Changbai Mountain area.

2. DATA AND METHODS

2.1 Study area

Antu County is located in Yanbian Prefecture, Jilin Province, at the northern foot of Changbai Mountain. The location of the study area and the distribution of main mineral springs are shown in Figure 1.

[Insert Figure 1]

The climate of study area has a temperate monsoon sub-humid climate with long winters and short summers. The average monthly climate change is shown in Figure 2. The annual average temperature is 4.0°C, and the annual average precipitation is 752.43mm. Temperature and precipitation show a uniform trend of change. But the annual distribution of precipitation is uneven. About 60% of the precipitation is concentrated in July and August, and it shows a decreasing trend from south to north in space. The annual average evaporation is 761.11mm, and the evaporation reaches its maximum value in April. Except for June and August, the evaporation value is larger than the precipitation value.

[Insert Figure 2]

The water system in this area is developed, all of which originates from Changbai Mountain and belongs to Songhua River system. The river valleys are deep and narrow with steep riverbed, rapid water flow and rich water resources. There are mainly Toutoubai River, Erdaobai River and Sandaobai River, etc. The rivers are roughly parallel from west to east and flow into Erdao Songjiang River. Among them, Erdaobai river originates from Tianchi of Changbai Mountain, with a total length of 104.9km, river slope of 6.8‰ and total watershed area of 2933 km^2. It is a mountainous river with winding river course, steep slope and rapid flow, steep banks and large drop gap. From south to north, the terrain on both sides gradually opens up and there is a large area of forest.

The terrain of the study area is high in the south and low in the north. Its highest point is located near Huangsongpu Forest Farm with an elevation of 1308m, and its lowest point is located north of Hongfeng Spring in the north with an elevation of 685m. Under the influence of multi-stage tectonics, the geological structures in the area are complex. The Xinghua-Baitou Mountain Tianchi fault zone is mainly developed in this area. And the type of topography is mainly erosional volcanic lava mountain platform, erosional tectonic mountain, intermountain denudation basin and intermountain valley plain. The main strata is the Neozoic Quaternary Lower Pleistocene System, and the covered rock is the lava riocks of Junjian mountain group(βQ_1).

Groundwater type in the area is complete, including fracture pore water of clastic rock, carbonate fissure-cavern water, basalt pore fissure water, loose rock pore water and bedrock fissure water. The distribution of basalt pore fissure water is widespread. And it is closely related to the occurrence and formation of mineral springs with fracture pore water of clastic rock

At present, 106 springs have been found in Antu County, among which 27 springs have been surveyed and evaluated. The main distribution locations of the mineral springs are shown in Figure 1. Most of the mineral springs are located near rivers. In the proved mineral water resources, the main type is metasilicic acid and a few are rare compound mineral springs enriched in CO_2. Abundant precipitation in study area provides amount guarantee for the formation of mineral water. The extensive distribution of metasilicate basalt in the area makes groundwater form mineral water which is rich in metasilic acid through the runoff process. The existence of fracture and lush vegetation provide a good migration, cultivation and storage condition for the formation of high-quality mineral water.

Since 2013, Antu County has engaged in the protection and management work of mineral water resources, and introduced a large number of enterprises into production with an annual output of 601,000 m^3. With the continuous development of mineral water and increasing construction, to ensure sustainable utilization of water resources and maintain its forming conditions and water quality is very important. Under the condition of mass exploitation in the future, the impact on other water bodies such as surface water resource can not be ignored. Thus, exploring the relationship between surface water and mineral water is of vital importance in the study area.

2.2 Data collection

A total of 57 water samples were collected for hydrochemistry and isotope analysis including mineral water, surface water and precipitation (Figure 3).

According to the distribution location and types of mineral springs and the flow direction of river, mineral and surface water samples were collected in July and October. 500ml-polyethylene bottles were used to collect water samples. After field work, the bottles were sealed, stored at 4°C and transported to the laboratory for test in the shortest time.

[Insert Figure 3]

2.3 Analysis methods

Electrical conductivity (EC) and water temperature were measured by handled electrical conductivity meter at the field sites. The chemical composition and stable isotope (^{18}O、D) were measured by the Public Technology Service Center of Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences. The cations and SO_4^{2-} were measured by inductively coupled plasma emission spectrometer (ICP-7500, Agilent Technologies Inc., USA), and the detection limit was less than 10μg/L. Other anions were measured by titration, and the detection limit was 1mg/L. All the detection accuracy is 5%. Anion balance verification is carried out to ensure that the error range of credibility is ±10%. The hydrogen and oxygen isotopes were measured by stable isotope mass spectrometer (MAT253, Thermo Finnigan Inc., USA) and the determination accuracy of δD and $\delta^{18}O$ is ±2‰. The results were reported in per mil deviation relative to VSMOW standard:

$$\delta=\left(\frac{R_{Sample}-R_{VSMOW}}{R_{VSMOW}}-1\right)\times 1000\,‰ \qquad (1)$$

where R_{sample} is the ratio of D/H or $^{18}O/^{16}O$ in water samples, and R_{VSMOW} is the ratio of D/H or $^{18}O/^{16}O$ of VSMOW standard.

The professional statistical analysis function of SPSS was used to the maximum value, average value and standard deviation of hydrochemical data. Through Aquachem, Piper diagram was drawn to analyze hydrochemical type of water samples. And Gibbs diagram was made to analyze the source of main chemical components.

Based on isotopic mass conservation, end elements are divided to calculate the conversion ratio of different water bodies. The calculation formula of two-end element method is as follows:

$$f_A=\frac{\delta_{mix}-\delta_B}{\delta_A-\delta_B} \qquad (2)$$

$$f_B=1-f_A \qquad (3)$$

where,$f_A$is the proportion of water A, f_B is the proportion of water B, δ_{mix} is δD or $\delta^{18}O$ of water mixed by A and B.

3 RESULTS AND DISCUSSION

3.1 Hydrochemical characteristics

3.1.1 Characteristics of electricity conductivity (EC) and temperature in water samples

Conductivity (EC) is an overall reflection of the total dissolved ion content in water. In the process of water transport, soluble rocks will be dissolved continuously and ion exchange will take place in surrounding rocks and soil. To a certain extent, it reflects the runoff path and retention time of water flow in the regional water cycle(Song et al., 2006).

As shown in Figure 4, EC value of mineral water in July is 84~1718μs/cm and of surface water is 117~165μs/cm. In October, EC value is 90~1680μs/cm and 120~190μs/cm respectively. On the whole, the EC of surface water fluctuates more in different months and in October it is slightly higher than that in July. That is because there is more precipitation in summer and the river runoff becomes larger, which will dilute the concentration of chemical components. The differences of EC among different mineral water is small and the overall EC is smaller than that of river water due to more intensive evaporation of surface water. There are two mineral springs with abnormally high EC value, namely Q-1-1 and Q-2-4. The main reason for this phenomenon is that the two springs are both compound mineral springs rich in CO_2 and the high content of HCO_3^- leads to the increase in the total dissolved ion content in the water. So the EC is much higher than others.

[Insert Figure 4]

Water temperature in July is higher than that in October, which is in line with the law of climate change in the study area. Surface water is warmer than mineral water. The reason may be that mineral springs are generally distributed in the forest areas with high vegetation coverage, which leads to less direct sunlight. And the change of ground temperature has slight impact on the underground temperature. So the water temperature is lower and the change range is small. As a hot spring, Q-2-4 has the highest temperature and its temperature maintain at a certain level all the year and is almost not affected by climate change. Surface water exposed to the sunlight directly, so it is greatly affected by climate change and the change of water temperature is more obvious.

3.1.2 Main hydrochemistry characteristics

The hydrochemistry data of mineral water collected from 2016 to 2019 are summarized. The results are shown in Table I.

[Insert Table I]

Mineral water in the study area is alkalescence. pH range is 6.96~7.89 with the perennial average is 7.34. TDS is at a low salinity level ranging from 93.8 to 188.0mg/L, with an average value of 131.80mg/L. The metasilicic acid concentration of each spring point conforms to the provisions in the “National Standard for Food Safety -- Drinking Natural Mineral Water”(GB8537-2018) and meets the standard for metasilicic acid content of mineral water (25mg/L). The content of metasilicic acid range from 49.6 to 59.13mg/L, and the average value is up to 55.37mg /L. There is a small difference in the content of cations. The average values of K^+, Na^+, Ca^{2+} and $Mg^{2+}$are 2.83 mg/L, 8.26 mg/L, 6.77 mg/L and 4.53 mg/L respectively. In anion, HCO_3^- is dominant with a perennial average of 59.78 mg/L. The concentration of F^- range is 0.38~1.77 mg/L. The maximum F^- concentration of Q-3-3 in 2018 and 2019 exceeds 1 mg/L, the value is 1.34 mg/L and 1.77 mg/L respectively. Cl^- concentration of two springs is also higher than that in other years. The reason is in the volcanic area the release of Cl^- and F^- is closely related to the deep magmatic activity and magmatic degassing. When the content of both is positively correlated, it indicates that the source of the spring is related to the degassing of the deep magmatic sac(Lin et al., 1999). The variation trend of TDS is consistent with that of HCO_3^-, which indicates HCO_3^- is the main factor affecting TDS.

As shown in Figure 5, the perennial variation coefficient and of the main components in mineral water is shown. It can be seen that the variation degree of pH and characteristic component metasilic acid relatively stable. The variation degree of TDS is the largest, which is mainly affected by the content of HCO_3^- and the strength of water-rock interaction during runoff process.

[Insert Figure 5]

The hydrochemical data of mineral water and surface water collected in 2020 are summarized. The statistical results are shown in Table II.

[Insert Table II]

The pH range of surface water is 7.20~7.76 and the average value was 7.41 with a small fluctuation. TDS is at a low salinity level with a range of 98.0~182.0mg/L and an average of 123.57mg/L, which is slightly lower than mineral water. The variation range of metasilicic acid concentration is 23.89~52.38mg/L and the average value is 43.01mg /L. Except for B-1, all the other surface waters reach the standard of metasilicate acid content of 25 mg/L. The F^- concentration varies from 0.47 to 1.56mg /L with an average of 1.01mg/L, which is slightly higher than that of mineral water. The highest F^- concentration is B-3-1, which is close to Q-3-3. There may be a hydraulic connection between them making the F^- concentration high and close. Different from mineral water, Na^+ has the most obvious advantage among cations in surface water with an average value of 17.08 mg/L. The dominant anion is HCO_3^- , which is as same as spring water, and with an average value of 71.52mg/L.

3.1.3 Hydrochmical type and source of main ions

The Piper diagram was made by using Aquachem software to analyze the hydrochemical types of surface water and mineral water, as shown in Figure 6.

[Insert Figure 6]

The distribution of anions in surface water and mineral water in different watersheds is relatively concentrated. The main anion is HCO_3^-. But cations are relatively dispersed and the hydrochemical types of surface water and spring water in each watershed are greatly different.

Among them, the cations of spring water in Toudaobai river watershed are obviously inclined to Mg^{2+} and the hydrochemical type is HCO_3-Mg. While the cations of surface water fall in the middle of Piper diagram with no obvious dominant cations, the hydrochemical type is HCO_3-Na-Mg-Ca. In Erdaobai river watershed, there are some differences in the hydrochemical types among water samples. The cations of surface water fall in the lower right part of Piper diagram, The main cation is Na^+. The hydrochemical type is HCO_3-Na. Most of the cations in the spring fall in the middle of Piper diagram with no obvious dominant cations. The hydrochemical type is HCO_3-Na-Mg-Ca. But as a compound mineral spring, Q-2-4 is significantly deviated from the distribution position of other springs in the Piper diagram. The cations fall in the left side and the main cation is Ca^{2+}. The hydrochemical type is HCO_3-Ca. The hydrochemical types of surface water in Sandaobai river watershed change along with the flow direction. The main cation in the upper and middle reaches is Na^+, and there is no dominant cations in the lower reaches. The hydrochemical type changes from HCO_3-Na to HCO_3-Na-Mg-Ca, indicating that more Ca^{2+} and Mg^{2+} are dissolved due to the change of environmental conditions. Most of the cations in the springs fall in the middle and the dominant cations are not obvious. The hydrochemical type is HCO_3-Na-Mg-Ca.

Gibbs diagram can be used to quantitatively describe the sources of ions in water by reflecting the dominant processes of precipitation, rock weathering or evaporation(Gibbs, 1970). Gibbs diagrams of water samples in study area are shown in Figure 7.

[Insert Figure 7]

From Figure 7, it can be seen that most of the surface water and metasilicate mineral springs fall in the middle of the figure. The ions mainly come from the weathering release of rocks. The two compound mineral springs fall on the top of the figures and outside the distribution model. There is no evaporation conditions for the location of two springs, so the source of ions may be the deep underground water after a strong water cycle and water-rock interaction.

3.2 Stable isotopic characteristics

The hydrogen and oxygen isotopic relationships of precipitation, mineral water and surface water samples collected in 2020 are analyzed, as shown in Figure 8.

[Insert Figure 8]

3.2.1 Precipitation

It can be seen from the Figure 8 that the precipitation points fall below the local meteoric water line (LMWL). The isotope of two precipitation samples in July is more enriched than that in October, mainly for the following reasons.

First, the re-evaporation of precipitation will affect the slope of the precipitation line. This is because the air humidity of the atmosphere or near-earth gas layer that the precipitation passes through is very low, which makes the precipitation vaporize when it reaches the ground. The precipitation may exchange isotopes with the rising water vapor in the clouds, resulting in the change of isotopic composition.

Second, the sources of water vapor in the study area in summer are mainly local water vapor in the west and northwest directions, as well as the water vapor brought by the monsoon from the Pacific Ocean. Due to the generally high temperature and strong evaporation in the interior of the continent in summer, lakes and rivers in the interior of the continent have absorbed most of the local water vapor(Cui, 1995; Li et al., 2012). So the $\delta^{18}O$ of precipitation brought by terrestrial water vapor from the northwest and local re-evaporating water vapor is relatively high. In autumn, sources of water vapor are mainly the polar Arctic Ocean moisture and the Atlantic ocean moisture transported by westerlies(Li et al., 2012). Influenced by monsoon climate, the air mass from the ocean in the whole northeast region from May to October is characterized by high humidity, weak evaporation and high precipitation. So during this period $\delta^{18}O$ has smaller fluctuation..

In addition, affected by temperature effect(Clark & Fritz, 1997), the moisture content in the air and the water vapor pressure increase with the increase of temperature, $\delta^{18}O$ values also increase. In July the temperature is higher than in October, therefore isotopes are more enriched.

3.2.2 Surface water and mineral water

In July and October, there is no obvious difference between the isotopic composition of Erdaobai river and Sandaobai river. So the supply conditions and evaporation intensity did not change much. Isotopes of Sandaobai river are close to LMWL, indicating that the river is mainly recharged by atmospheric precipitation and is less affected by evaporation. Caused by evaporation, Erdaobai river deviate from LMWL slightly, but the slope and deuterium surplus (d) value is close to it. Isotopes of two river enrich and d values decrease gradually along the flow direction, indicating the river is a continuous flow, and the water body has certain variability. The evaporation influence during the flow process is different and unbalanced, and the water cycle becomes more intense along the flow direction.

There is a big difference between the isotopic enrichment degree of Toutaobai river and mineral water. In July, Toutaobai river fall on the lower right of LMWL and is far away from it, indicating that it is also recharged by other supplies except atmospheric precipitation. It might be the glacier melting snow of Changbai Mountain. The isotope of Toudaobai river is the most enriched, and the d value is negative. This phenomenon always appears in the arid region(Gu et al., 1998). But the climate in the study area is sub-humid climate and the water vapor is rich. For the abnormal phenomenon, climate factors can be ruled out. It may be due to the long recharge path and slow runoff process, which makes the interaction with the surrounding rocks is intensive. And there may occur secondary evaporation during the recharge process. However, the isotope of Toudaobai River falls near the LMWL in October, indicating an obvious change in the recharge source. Atmospheric precipitation recharge has a certain delay. After the precipitation concentration period in July and August(Figure 2), the supply source changed from glacier melting to precipitation, leading to changes in the isotopic composition.

Isotopes of mineral water in July fall in the lower left corner, above the LMWL. Slope of δD-$\delta^{18}O$ fitting line is 3.31, less than atmospheric precipitation line slope 7.77. d value ranges 11.56~15.89. Along with the flow direction, the change law is not significant, indicating the recharged degree of each mineral spring is different. Some mineral spring may be recharged by deep underground water, and in the infiltration process of atmospheric precipitation, evaporation and water-rock interaction will happen. In October, isotope composition is more enriched and close to the isotope composition of LMWL and surface water, indicating the recharge supply changes into precipitation. Combining EC and ions change of surface water and mineral water, it can be preliminarily determined that there are frequent mutual transformation processes between them.

3.3 Analysis of relationship between surface water and mineral water

In combination with the hydrochemical characteristics of water bodies in the study area, the characteristic components of mineral water, metasilicic acid (H_2SiO_3) and the conventional ion Cl^- are used as tracers. Due to the slow cycling rate of mineral water, δD and $\delta^{18}O$ are in a low value state compared with surface water. When the isotope values change, the transformation relationship between different water bodies can also be revealed.

3.3.1 Toudaobai river watershed

The tracing component content of mineral water and surface water in Toudaobai River watershed is shown in Figure 9.

[Insert Figure 9]

From Figure 9, there is a large difference of isotopic composition between Q-1-1 and B-1 in July. In October, the isotopic compositions of the two points are similar, but the Cl^- concentration of Q-1-1 is 18.46mg/L, and the concentration of H_2SiO_3 is 111.74mg/L. The corresponding concentrations of B-1 are 9.66mg/L and 23.89mg/L, respectively.

Combined with the actual situation, Q-1-1 locates at a high altitude and is rich in CO_2. Therefore, its hydraulic connection with surface water is weak. In July and October the main recharge source of mineral water and surface water is greatly change. After concentrated period of precipitation, the recharge sources of Q-1-1 change from atmospheric precipitation and underground water mainly to atmospheric precipitation.

3.3.2 Erdaobai river watershed

The tracing component content of mineral water and surface water in Erdaobai River watershed is shown in Figure 10.

[Insert Figure 10]

From Figure 10, Cl^- content of the surface water in Erdaobaihe River basin is greater than that of mineral water, and the content of H_2SiO_3 is less than that of mineral water. $\delta^{18}O$ is enriched. There is oxygen shifting along the flow direction. Cl^- content of mineral water also presents an increasing trend, and the upstream isotope is more enriched than downstream. The variation of H_2SiO_3 in mineral water is small and shows an increasing trend, but the concentration of H_2SiO_3 in surface water decreases. On the whole, isotopes and hydrochemistry show a uniform trend of change. According to equation (2), the recharge proportion of mineral water to surface water is about 61%. The isotopic composition and change of surface water in October are same as that in July. Although the isotopic of mineral water is enriched obviously compared with that in July, the variation trend is opposite to that of surface water. And there is also a certain difference in hydrochemical change. Therefore, the hydraulic connection between the two is weak in October.

3.3.2 Sandaobai river watershed

The tracing component content of mineral water and surface water in Sandaobai River watershed is shown in Figure 11.

[Insert Figure 11]

It can be seen from Figure 11, in July the other components content of surface water are higher than that of mineral water except for H_2SiO_3, among which $\delta^{18}O$ is consistent with the change trend of Cl^-. According to equation (2), the recharge proportion of mineral water to surface water is about 69%.

In October, the contents of H_2SiO_3 and Cl^- in surface water and mineral water change little, but $\delta^{18}O$ shows great difference. The change trend between surface water and mineral water is opposite, which was consistent with the rule of Erdaobaihe river watershed. The interaction between surface water and mineral water is weak in October.

From the above analysis, it can be seen that the hydraulic connection between surface water and mineral water is weak in different periods in Toutaobai river watershed. But there is an obvious interaction between mineral water and surface water in Erdaobai river watershed and Sandaobai river watershed, as shown in Figure 12.

[Insert Figure 12]

Mineral water recharges surface water in July, and the recharge ratio is more than 60%. Precipitation has an obvious lag effect on the recharge of mineral water and surface water. After the concentrated precipitation in July and August, the hydrogen and oxygen isotopes of surface water and mineral spring in all watersheds in October are obviously close to the local meteoric water line, and the main recharge sources are mainly precipitation. Therefore, mineral water is one of the main factors affecting the amount of surface water resources in summer. In the process of mineral water resources development, it is necessary to pay attention to the change of river flow to avoid the damage of regional water resources balance caused by excessive development.

4 CONCLUSIONS

A combined application of hydrchemical indicators and stable environment isotope characterization are performed to study the mineral water and surface water in Changbai Mountain area. The conclusive remarks are summarized as follows:

In the study area, EC changes little in summer and autumn and EC of surface water is slightly higher than that of mineral water. Besides, EC changes slightly along the flow direction of groundwater and surface water. Temperature change conforms to the climate change characteristic.

The annual fluctuation of surface water and mineral water hydrochemistry in the study area is relatively slight. The hydrochemical type of surface water is mainly HCO_3-Na, while the hydrochemical type of mineral water is mainly HCO_3-Na-Mg-Ca type. And it does not change significantly along the river flow direction. Most of the ions in mineral water mainly come from rock weathering. Ions of two compound mineral springs rich in CO_2 may be from deep groundwater through strong water circulation and water-rock interaction.

The main recharge source of water in study area is precipitation. Precipitation isotope deviates from LMWL and is rich in $\delta^{18}O$, which is affected by the water vapor source. Slopes of different δD-$\delta^{18}O$ relation lines are smaller than LMWL caused by evaporation. The isotopes of surface water are more enriched than mineral water. The water cycle and evaporation of surface water are more strongly.

The recharge sources of mineral water and surface water in different watersheds have changes in each period, and precipitation has a certain delayed effect to the replenishment of different water resource. In July, in addition to atmospheric precipitation, the Toudaobai River received the glacier melt snow supply of Changbai Mountain. The Erdaobai River and Sandaobai River receive the joint recharge of precipitation and mineral water and the recharge proportion is above 60%. In October, precipitation is the main source of water supply. Mineral water resource in summer is the main factor affecting the water amount. Therefore, in the process of mineral spring development, attention should be paid to the balance of other water resources to avoid excessive development.

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