AGE DATING OF THE GROUNDWATER IN THE SPRING AREA OF JINAN CITY

Fang Peixian*   Cao Yuqing*   Tang Kewang*
Li Xiangzhi**   Wang Shaowen**

* Changchun College of Geology, Changchun, Jilin, China
** No. 801 Hydrogeological Party, Shandong Bureau of Geology and Mineral Resources, China

ABSTRACT

In this paper the analysis of the environmental isotopes is used to estimate the age of groundwater in the spring area of Jinan City; the chemical age of spring water is estimated from the theory of dissolution dynamics on carbonate minerals; and finally a comparison is made between the chemical and isotopic ages.

HYDROGEOLOGICAL SETTING OF THE SPRING AREA

The relief of the spring area in Jinan is high in the south and low in the north. It rests against the Taishan Mts. in the south and is contiguous to the Qihe-Guangrao fault in the north, thus being located in between the Luxi (W. Shandong) uplift and Luxibei (NW Shandong) depression. It is a monoclinal structure dipping northward and mainly composed of the Paleozoic strata.

The strata in the region are northerly-younging and dip northward. From south to north there are distributed the migmatitic granitic gneiss of the Archean Taishan Group, the Cambrian limestone, sandstone and shale, the Ordovician carbonate rocks, coal seams and Quaternary deposits. The aquifers comprise phreatic water in the weathering fissure zones of metamorphites, karst-
fissure water in the Zhangxia Formation, fissure karst water in the Fengshan Formation and Ordovician carbonate rocks, and porous water in the Quaternary unconsolidated formation, of which the fissure karst water in the Fengshan Formation-Ordovician carbonate rocks is widely distributed, of better water-enrichment, and responsible for the spring group. The groundwater is directly recharged from the precipitation or river water seepage in the exposed bedrock area in the south, and its flow to the north is blocked by a magmatic rock body and hence discharges in the form of springs in the urban district of Jinan. There are four large fissure-karst spring groups: Baotu, Heihu, Wulong and Zhenzhu springs, making Jinan City a famous "spring town" in China.

The boundary conditions of the karstic aquifer in the area are impervious except for the western part where there are permeable boundaries, making the aquifer an independent moving system (see Fig.1).

THE ESTIMATE OF THE ISOTOPIC AGE OF GROUNDWATER

For the study of karst water in the area, 19 groundwater samples, 2 rainfall water samples and 2 surface water samples were collected in 1985. All samples were analysed for $\delta^{18}O$, $\delta^D$ and $^3H$. Based on the results of the analysis, age determinations of groundwater in the area were made. The sampling sites are shown in Fig.1.
Analysis of the Stable Hydrogen and Oxygen Isotopes

According to the experimental data, the $\delta^{18}O$ value of the groundwater in the area ranges from $-8.0\%$ to $-9.5\%$, while the $\delta D$ value commonly ranges from $-54\%$ to $-70\%$. The figures are close to each other, indicating the same origin of the groundwater.

The dash line in Fig.2 represents the regression line for groundwater samples. The regression equation is:

$$\delta D = 6.5 \times \delta^{18}O - 5.1$$

$$\left( y = 0.6114 > y_{0.01} \right)$$

It can be seen from Fig.2 that the regression line for groundwater is roughly below the "precipitation line" ($\delta D = 8 \times \delta^{18}O + 10$). Since the value of $\delta D$ basically represents the content of local rain or surface water, the groundwater in this region must be originated from the percolation of precipitation. However, the phenomenon of "Oxygen shift" occurs for most groundwater samples. The "Oxygen shift" is introduced here as a reference index:

$$\Delta \delta^{18}O = \delta^{18}O - (\delta D - 10)/8 \quad \text{(1)}$$

where $\delta D$ and $\delta^{18}O$ are the measured values for the groundwater samples. The $\Delta \delta^{18}O$ obtained is the "Oxygen shift" relative to "precipitation line". Now a relevant discussion is made as follows.

The solid circles in Fig.2 represent water samples from the recharge area, and are classified into two types according to the values of oxygen shift. The one is with the oxygen shift value $\Delta \delta^{18}O$ of about $-3\%$ shown in Fig. 2 (e.g. Nos 1, 3, 7, 9 which are distributed on the "precipitation line"). These samples were collected from the slope of the mountain area where the groundwater level is buried at a small depth, the flow is quicker and groundwater level is affected by local seasonal
precipitation water. The other solid circles are also located in the recharge area where groundwater is in the transition zone between the recharge and confined areas, where groundwater circulation is deeper. These samples represent the groundwater coming from both the upstream flow and local precipitation water. Therefore, it is a mixed water body formed by repeated and even perennial precipitation, with an oxygen shift of 0.2‰. These samples are distributed near the "precipitation line". Some deeper circulated sample points such as points Nos. 4 and 5, have a higher $\Delta^{18}O$ value of 4-5‰ and deviate from the "precipitation line".

Fig. 3 Sections of outcrops of springs

The crosses (x) in Fig. 2 represent groundwater in confined area (or runoff area) where the terrain is gently sloped and the aquifer is buried at a greater depth with a greater thickness and a higher $\Delta^{18}O$ value averaging 0.4‰ and on the whole higher than that of the water samples from the recharge area. The open triangles "Δ" in Fig. 2 represent the water samples from the discharge points. The values of $\Delta^{18}O$ in
the Baotu, Heihu and Wulongtan springs are 0.1004%, 0.3924% and 0.7928%, respectively at the concentration discharge points. Their values indicate the circulation depth and burial conditions of the water of each spring. As shown in Fig.3, the water in the Baotu Spring is the shallowest and that of the Wulong Spring is the deepest.

The above facts show that the values of oxygen shift reflect the duration of groundwater movement in the aquifer. The "oxygen shift" occurs when soluble rocks rich in $^{18}O$ are continuously dissolved by karst groundwater to make the content of $^{18}O$ in the water shift relative to the original state ($\delta^{18}O$ in precipitation water). In addition, the isotope exchange between groundwater and rock may also account for the oxygen shift, the longer the groundwater contacts with the rocks, the greater the exchange quantity is. The results of the study, the fractional coefficient between CaCO$_3$ and water is 1.031 at 25°C. Therefore, it is suggested that the age of the Baotu Spring water is less than that of the Heihu Spring and the age of the Heihu Spring water should be less than that of the Wulongtan Spring water.

**The Estimate of Tritium Isotope Age of Groundwater**

1. The determination of the model

The total area of Jinan spring group in Jinan is 1430 km$^2$. The groundwater system receives rainfall recharge over a large area. In the process of northward flow, the fissure-karst water is continuously mixed fully with the precipitation water and seepage of surface water in the recharge area. The groundwater flow is blocked by igneous rocks in the urban district and discharged in the form of springs (Fig.1). Therefore, the spring water represents the combined output of repeated rainfall or perennial rainfall. This mixed pattern belongs to the complete mixing type. The average of tritium in groundwater is close to the output value of tritium of the spring water, permitting the use of the complete mixed model to estimate the delay time of the spring group in Jinan.

For the complete mixed model, when the input function $C_{in}(t)$ of the isotope for the ground water
system is known, according to the law of mass conservation, the output concentration may be expressed as:

\[ C_{\text{out}}(t) = \int_0^\infty C_{\text{in}}(t-\tau)e^{-\lambda\tau}g(\tau)d\tau \quad \ldots \ldots \ldots (2) \]

\[ g(\tau) = \frac{1}{T}e^{-\tau/T} \]

where:
- \( C_{\text{out}}(t) \) -- isotope concentration in the output time series
- \( C_{\text{in}}(t-\tau) \) -- isotope concentration in the input time series
- \( e^{-\lambda\tau} \) -- the corrected value of the decay
- \( g(\tau) \) -- the proportion of groundwater whose age is \( \tau \)
- \( \tau \) -- the time of stagnation of water in the system
- \( t \) -- sampling time
- \( T \) -- the average stagnation time of groundwater

Equation (2) can be expressed as:

\[ C_{\text{out}}(t) = \sum_{\tau=0}^{\infty} C_{\text{in}}(t-\tau)e^{-\lambda\tau}(1/T)e^{-\tau/T} \ldots \ldots \ldots (3) \]

Since the samples were taken in 1985, \( t \) in the model is 1985, when \( \tau \) is 32 years, \( (t-\tau) \) should be 1953. Since the tritium value in the global rainfall was less than 10 TU before 1953, the model is finally simplified as:

\[ C_{\text{out}}(t) = \frac{1}{T} \sum_{\tau=0}^{32} C_{\text{in}}(t-\tau)e^{-\tau}(1/18+1/T) \ldots \ldots (4) \]

(2) Input function and the result of calculation
For the lack of systematic observation of the data on the tritium in the rainfall in China, the input tritium value in Jinan City was interpolated by using the distribution pattern of the tritium in the global
rainfall (e.g. in Ottawa, Hongkong & Irkutsk), and then was weighted to correct for rainfall. The calculation was performed by equation (4), and $C_{\text{out}}(t)-T$ curve (Fig. 4) was made to obtain the average age of groundwater corresponding to the output concentration. The age of Baotu, water from the Heihu and Wulong springs obtained by the content of the tritium in the spring water is 25.67, 27 and 40 years, respectively. These ages are corresponding to the results of the stable isotope analysis.

THE DETERMINATION OF CHEMICAL AGE OF GROUNDWATER

In the region, the soluble rocks are widely distributed and composed mainly of calcite, dolomite and gypsum. So the carbonate--sulphate solution reaction formulas are:

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 & p_{k0} (25^\circ\text{C}) = 1.47 \\
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- & p_{k1} (25^\circ\text{C}) = 6.35 \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_2^2- & p_{k2} (25^\circ\text{C}) = 10.33 \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- & p_{kw} (25^\circ\text{C}) = 14.00 \\
\text{CaCO}_3 & \rightleftharpoons \text{Ca}^{2+} + \text{CO}_2^2- & p_{kC} (25^\circ\text{C}) = 8.35 \\
\text{CaMg(CO}_3)_2 & \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^2 + 2\text{CO}_3^- & p_{kd} (25^\circ\text{C}) = 16.50 \\
\text{CaSO}_4\cdot 2\text{H}_2\text{O} & \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} & p_{kg} (25^\circ\text{C}) = 4.61
\end{align*}
\]

According to the law of mass action, the model of chemical reaction rate is:

\[
\begin{align*}
\frac{d\text{a}_{\text{ca}}}{dt} &= k_{c}(1-\beta_{c}) + k_{d}(1-\beta_{d}) + k_{g}(1-\beta_{g}) \\
\frac{d\text{a}_{\text{mg}}}{dt} &= k_{d}(1-\beta_{d}) \\
\frac{d\text{a}_{\text{so4}}}{dt} &= k_{g}(1-\beta_{g})
\end{align*}
\]
Based on equation(5) and the initial conditions chemical age can be determined by the matching method.

The basic idea of this method is that some groups of drillholes with small spacing and data of water level, pumping test and hydrochemistry are selected and the calculation is performed as follows.

1. The determination of k value by matching method when age is known
   (1) Time $t$ is obtained from Darcy Law by $\Delta h$ (level difference), $\Delta s$ (distance) and K value (permeability coefficient).
   (2) The ion concentration in two holes upstream and downstream is taken as the initial and terminal concentrations, and the values of $t, \beta_c, \beta_d$ and $\beta_g$ obtained are substituted into the differential equation.
   (3) The values of $k_c$, $k_d$ and $k_g$ are matched and obtained by using fourth-order Longer-Kuda method.
   (4) The arithmetic averaging of K values of ions from each spring area is conducted on each block and then on the whole region to obtain the values of $k_{ccp}$, $k_{dcp}$ and $k_{gcp}$ for the ions of the corresponding area.

2. The determination of chemical age of each spring in the spring area are obtained using the known $k_{ccp}$ values
   (1) The contents of the ions in the rainfall and spring water obtained from the chemical analysis are taken for the initial and terminal concentrations of the related ions, and the obtained $k_{ccp}$, $k_{dcp}$, $k_{gcp}$, $\beta_c, \beta_d$ & $\beta_g$ are substituted into the differential equation.
   (2) The value of $t$ is matched and obtained by fourth-order Longer-Kuda method.
   (3) The corresponding $t$ values for each related ion are obtained, the arithmetic average $t_{ccp}$ of them is taken for the chemical age of the corresponding spring water.

The results of the calculation are as follows: For Baotu Spring: the age of $Ca^{2+}$, $Mg^{2+}$ and $SO_4^{2-}$ is 19.25, 21.03 & 21.22 years respectively, averaging 20.50 years; For Heihu Spring: 24.70, 26.35 & 25.91 years respectively, averaging 25.65 years.
CONCLUSIONS

The following conclusions may be drawn from the above analysis and calculation:

(1) The result of the stable isotope analysis shows that the groundwater in Jinan spring water system comes from the infiltration of precipitation water, justifying traditional consideration.

(2) The different exposure conditions, stable isotope analysis and isotope age calculations for every spring group have shown that the Baotu Spring water is of shallow circulation and Heihu Spring comes from the water of moderately-deep circulation, and has a longer time of migration of groundwater. The Wulong Spring comes from the deepest circulated water and its recharge source is the farthest, therefore its age is the oldest. This conclusion is fully consistent with geological conditions.

(3) The calculated chemical age is close to the isotopic age. Therefore, it is an effective method for determining the age of groundwater in karst aquifers with conventional analysis of information. Such an age and isotope age may be mutually complementary.

(4) The chemical age calculation is only a preliminary attempt and there are still some problems to be solved further.

REFERENCES


