



## Groundwater Renewal and Residence Time in Shiyang River Basin, Northwestern China

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### ABSTRACT

The age of groundwater is important in assessing renewability, recognizing movement and mass transport processes, and constraining model parameters of groundwater. In this study, we analysed the groundwater isotope ( $^3\text{H}$  and  $^{14}\text{C}$ ) of Shiyang River Basin, and estimated the groundwater age and its renewal rate. We found that the age of shallow groundwater in the Gobi zone was between five and ten years, and the age of groundwater in the piedmont region was about fifty years. However, the age of groundwater in the fine soil plain was more than fifty years, which was older than the groundwater in the Gobi zone and piedmont region. The renewal rate of shallow groundwater ranged from 0.0006% to 1.0% /a. In addition, the age of deep confined water shared an increased trend from the piedmont to rump. Specially, the youngest groundwater was in the piedmont with an age between 1000 and 2900 years, the groundwater age of the fine soil plain between 2920 and 3400 years, and the groundwater in rump region was more than 4000 years. The renewal rate of the deep groundwater was 0.0078-0.045% /a. The results suggested that shallow groundwater is younger than deep groundwater, and thus shallow groundwater is closely related to atmospheric precipitation with a shorter residence time and faster renewal rate than deep groundwater. In contrast to the shallow ratio of Zr/Mn, adsorbent dose and solution pH was investigated. The adsorption isotherm was emphatically investigated and thermodynamic parameters were calculated to better understand the adsorption mechanism.

### INTRODUCTION

In arid and semi-arid environments, water is the most important resource for sustaining life (Cheng et al. 2002, Yang et al. 2010) and studies of hydrological cycle processes have, therefore, received considerable attention (Shi et al. 2001, Feng et al. 2004). Surface water resources are generally scarce and highly uncertain in semi-arid and arid regions because groundwater is the primary source of water in these regions (Gates et al. 2008, Ma et al. 2009). Groundwater availability is a function of the local geology, which defines the occurrence of aquifers, their storage capacities, their recharge rates, the transmissibility between aquifers, and their natural water quality. Due to increasing groundwater exploitation, knowledge of the recharge rates and characteristics has become an important issue to safeguard the sustainable use of groundwater resources. In fact, groundwater recharge is often the most important parameter for the sustainability of ecosystems in arid and semi-arid areas (Wheater et al. 2000, Kinzelbach et al. 2003). However, it is difficult to estimate recharge using conventional water balance methods. Environmental isotopes in groundwater combined with chemistry can produce a more reliable conceptual model of

a groundwater system at both local and regional scales, especially in cases where little rainfall and high evaporation potential exist in arid regions (Herczeg et al. 2000, Scanlon et al. 2002, Mählknecht et al. 2004, Glynn et al. 2005, Zhu et al. 2008, Liu et al. 2014). Isotopes have also been used as a dating tool to identify the age of groundwater that recharged under the colder-than-current climates of the late Pleistocene (Edmunds et al. 2006, Su et al. 2009, Saeko et al. 2014).

Compared with other methods, groundwater dating has a distinct advantage when evaluating groundwater renewal ability. That is, it can be used for rapid determination and evaluation and long-term and reliable dynamic observation data of the underground water level and flow field do not need to be measured. Therefore, this is the fastest method (Yang et al. 2015). Age is an important indicator to identify natural underground water, as well as the coordinate axis of recourse of the origin and evolution of groundwater. Groundwater age is often thought to be stranded after the make-up water through the soil into the aquifer (Chen et al. 2004). In 1957, Munnich first evaluated the age of groundwater using  $^{14}\text{C}$ , and then established the basic

method. After years of development, the method has been continuously improved. At present, isotopes are important tool to determine groundwater age (Zhang et al. 1987, Narasimhan et al. 2005, Liu et al. 1997).

The Shiyang River Basin, located in the eastern part of the Hexi Corridor in the middle of Gansu province, Northwestern China, is considered a typical arid and semi-arid area. As a result of long-term water resource development, the Shiyang River Basin has become one of the most over-exploited inland basins. Water resource shortage is an increasingly serious issue in China, especially in the arid and semi-arid areas of the Northwest. The Shiyang River is an eco-environmentally fragile area, which is characterized by low and irregular rainfall, high temperatures and evaporation, and notable drought periods. Research of groundwater renewal and residence time in the ecological environment of the Shiyang River Basin is directly related to land desertification, sandstorm source area and major environmental problems such as frequency in arid areas. Therefore, it is important to identify the mechanism underlying the formation of a dry environment and the associated development process (Ding 2007a,b).

In this study, we investigated isotopes ( $^3\text{H}$  and  $^{14}\text{C}$ ) and discussed the age of the groundwater and renewal rate in the Shiyang River Basin. Our specific objectives were (1) to investigate the age of shallow groundwater using the  $^3\text{H}$  value, (2) to identify the age of deep confined water making use of  $^{14}\text{C}$ , and (3) to estimate the groundwater age and its renewal rate.

### Geology and Hydrogeology of the Study Area

The Shiyang River Basin is located at the eastern edge of the Hexi Corridor in the middle of Gansu province (Fig. 2). The Shiyang River originates from Lenglongling Glacier of the Qilian Mountains and ends gradually in the Tenggeli Desert. The Qilian Mts. form the southern part of the Basin. Many modern glaciers are distributed above 4,500 m. The middle and northern part of the Basin is a plain that can be divided into two sub-basins. Most of the Basin belongs to the arid climate zone. Solar radiation is strong and bright. Summers are hot and short, while winters are cold and long. The temperature difference is extremely significant. Low rainfall and evaporation intensity lead to dry air. The annual precipitation is 200-800 mm, while the evaporation capacity is 2000-3000 mm.

Consisting of Quaternary alluvial and pluvial sediments, the Wuwei Basin lies in a depression at the foot of the Qilian Mts. with an elevation ranging from 1,400-2,500 m. The loose Quaternary sediments filling the basin are of great thickness, and provide an ideal location for groundwater

preservation. In terms of the hydrogeological characteristics, two geomorphologic units are recognized in the Wuwei Basin, a faulting terrace zone and its sub-basin. The former is in the vicinity of Qilian Mts. and lies on the head of a pluvial fan. The aquifer is composed of gravel and sand. Well-connected porosity of the aquifer provides a good conduit for groundwater flow, which is the basin's recharge region. The sub-basin is the enrichment zone of the groundwater. As the grain size of the aquifer gradually decreases from south to north and the flow rate becomes slower, the hydraulic gradient becomes smaller. Along with the uplifting of the Quaternary basement, the burial depth of the aquifer becomes shallower, resulting in groundwater springs in the middle part of the Wuwei Basin (Fig. 1).

In the southern part of the Wuwei Basin, a diluvial aquifer is formed from highly permeable cobble and gravel deposits that are between 200 and 300 m thick. The aquifer specific capacity is about 3-30 L/(s-m), and aquifer permeability reaches 100-600 m/d. This allows a large amount of surface runoff in the piedmont fan to seep down and recharge the aquifer. From the northern edge of this diluvial fan, the aquifer, comprising interbedded cobble gravel, fine sand and clay, becomes confined or semi-confined with piezometric levels less than 5 m deep. In many places the groundwater overflows as springs and re-emerges as streams.

The limited precipitation in the plains of the river basin accounts for less than 7% of the total groundwater recharge. Hence, as found in other inland river basins in arid northwest China, the aquifer in Shiyang River Basin is, to a large extent recharged by surface water via river infiltration, canal system seepage and farmland irrigation water seepage. In other words, surface water and groundwater are integrated in the middle and lower basins, and the upper, middle and lower reaches are united in the use of water resources. The water resources in the different parts of the basin are inseparably linked: the groundwater resources in the plain area are recharged from precipitation in the Qilian Mountains. From the Qilian Mountain reach to the Hongyashan section, groundwater and surface water are closely linked due to the gradient and the uniquely permeable nature of the sediments near the mountains. To a large extent, the groundwater is transferred back to surface water before flowing out of the section. Surface water in the Hongyashan reservoir, therefore, mainly originates from surface water and spring water originally present as short residence time groundwater within the Wuwei Basin.

### MATERIALS AND METHODS

According to the topography, geomorphology and hydrogeology, 13 groups of sampling locations from Qilian

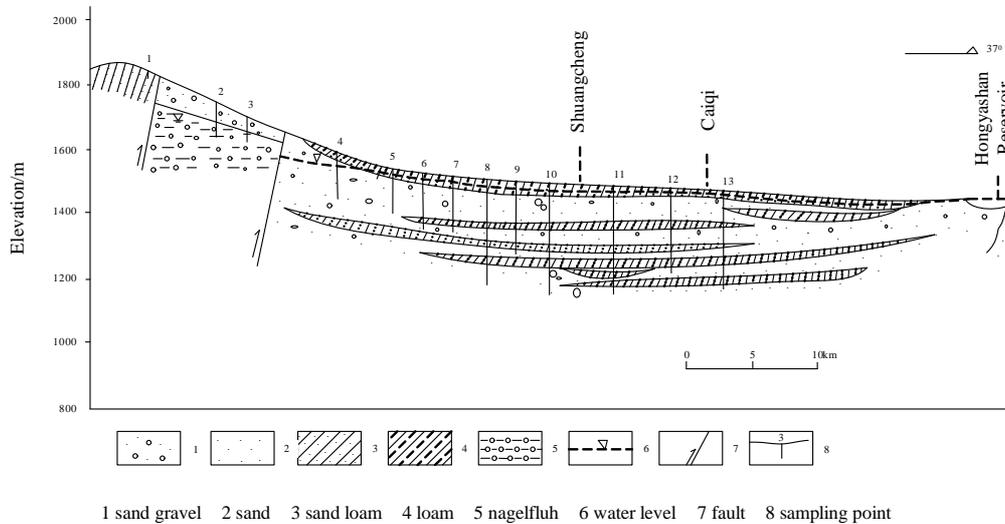


Fig. 1: Hydrogeological cross-section of the Wuwei Basin.

Mountain to Hongyashan Reservoir were chosen (Fig. 2). The sample point locations were positioned using a GPS locator. The well depth, latitude, longitude, groundwater depth, water temperature as well as pH value (pH) were measured on site. All water samples were packed in plastic bottles, which were then sealed with wax. Sample bottles were washed three times with the same water sample before they were filled. No air bubbles were allowed in the bottles to avoid exchanging with carbon dioxide in the air. All samples were filtered (0.45  $\mu\text{m}$  membrane filters), and an aliquot acidified with 1%  $\text{HNO}_3$  was used for preservation, for the analysis of cations and trace elements. Unacidified samples were collected for anion and stable isotope analysis. Unfiltered 2 L samples were collected for radiocarbon and  $^3\text{H}$  analysis.

Precipitation materials were collected from the global precipitation isotope which is established by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO). Tritium was tested by using a low background proportional counter plan after electrolytic enrichment, with unit TU. The precision for  $^3\text{H}$  was  $\pm 0.3$  TU, while the relative standard error of the method for higher  $^3\text{H}$  concentrations was below 10%. Tritium values were determined using a Low Background Liquid Scintillation Counter in the HeHai University state key laboratory of hydrology and water resources and water conservancy engineering science.  $^{14}\text{C}$  was measured using Liquid Scintillation Counter counts after samples were transformed into benzene, and was expressed in pmc. Carbon values were determined using the accelerator mass spectrometer laboratory at Beijing University. Percent modern C values (pmc) had  $1\sigma$  errors  $<0.3$  in all cases.  $\delta^{13}\text{C}$  was measured using a

stable isotope mass spectrometer with an overall analytical error of  $\pm 0.15$  ‰ based on repeated analysis of samples and standard materials.

## RESULTS AND DISCUSSION

### Tritium Date

The IAEA's network of pluviometer in Zhangye is the only station in northern China that can provide monthly precipitation  $^3\text{H}$  concentrations from 1983. According to the model developed, the  $^3\text{H}$  data have been reconstructed from 1953 to 1982 for Zhangye station and used as the local  $^3\text{H}$  data (Wei et al. 1980, Guan et al. 1986). The decayed precipitation record, which represents  $^3\text{H}$  concentration in groundwater that infiltrated between 1957 and 1996 was modified using a basic exponential decay equation using a half-life of 12.43a for  $^3\text{H}$  to reflect the mass loss through radioactive decay. The resultant groundwater  $^3\text{H}$  record can be used to assist in the interpretation of the regional groundwater flow system, providing a qualitative age indication (Ma et al. 2008).

The differential equation of the mass balance of tritium is:

$$C(t) = \int_0^\infty C_0(t-\tau)e^{-\lambda\tau} f(\tau) d\tau \quad \dots(1)$$

Where,  $C(t)$  is the output concentration of the tritium at time  $t$ ;  $C_0(t-\tau)$  is the input concentration; and  $f(\tau)$  is the age distribution function of groundwater.

The tritium spectrum is restored using mathematical statistical methods, atmospheric precipitation characteristics and date from the IAEA. The tritium recovery results are

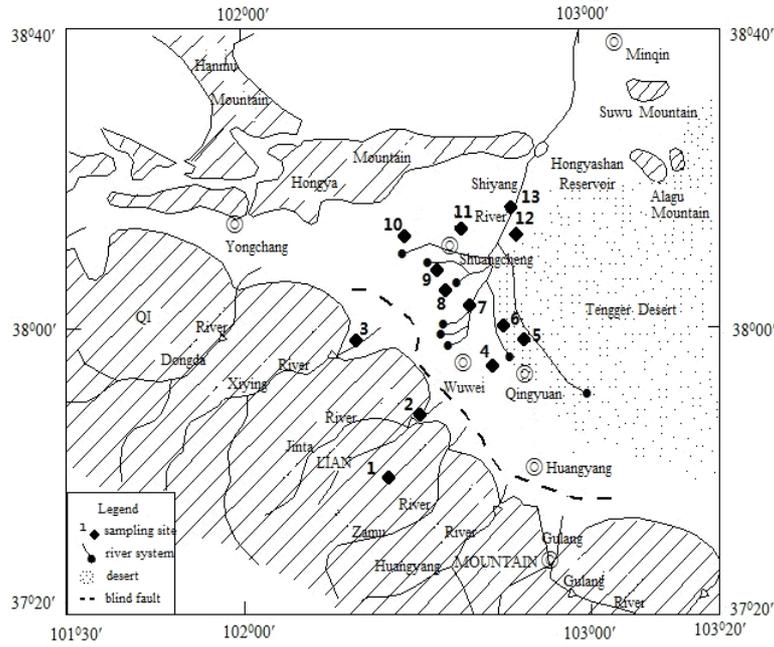


Fig. 2: Water quality sampling points.

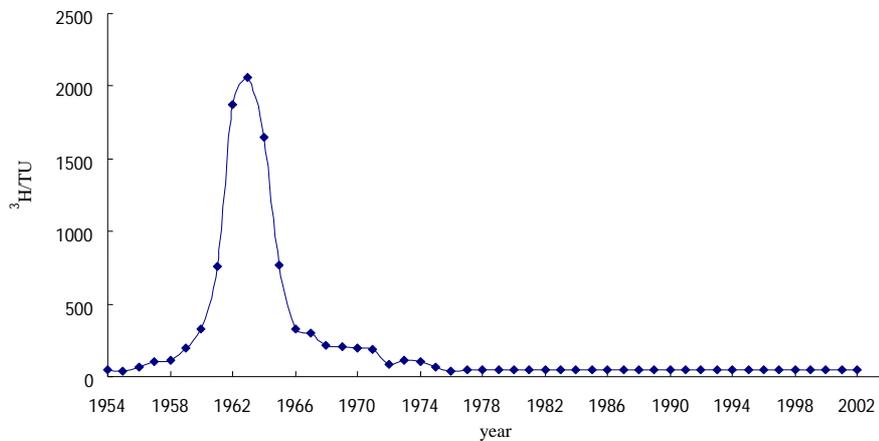


Fig. 3: Curve of tritium concentration in atmospheric precipitation.

presented in Fig. 3. The precipitation tritium values exhibited the following pattern: a slow increase in 1961, a rapid increase to the peak in 1963, a rapid decline in 1966 to the 1961 levels, followed by a slow annual decline with little change after the 1970s.

The  $^3\text{H}$  simulation values for groundwater in the study area are presented in Fig. 4. The tritium concentration showed a decreasing trend from the piedmont of the red cliff

mountain reservoirs. However, in Yongchang town in the central basin, the Baiyun sample tritium concentration was higher, possibly because at that location, irrigation and groundwater alternation is more active, and the groundwater contains freshwater supplies.

Groundwater age can be quantitatively estimated through a model (Zuber 1986,1994, Maloszewski et al. 1982, 1996). The groundwater system can be generalized into a linear sys-

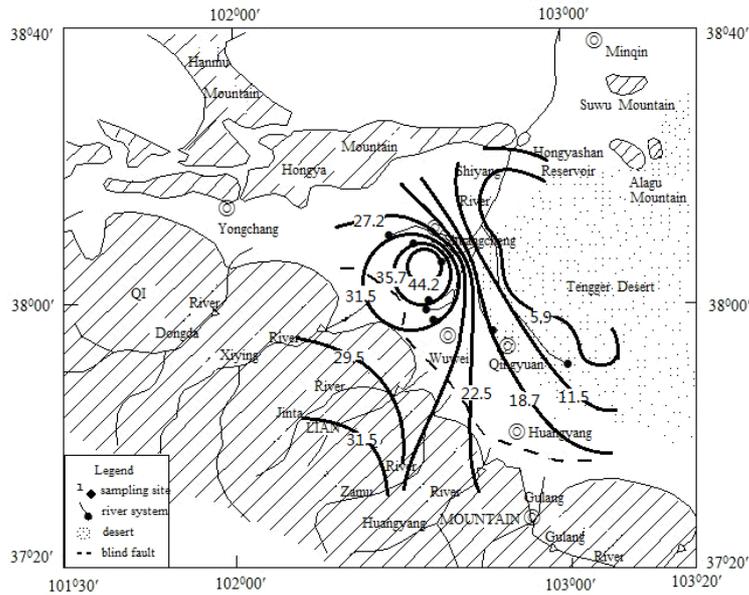


Fig. 4: The tritium simulation in the study area.

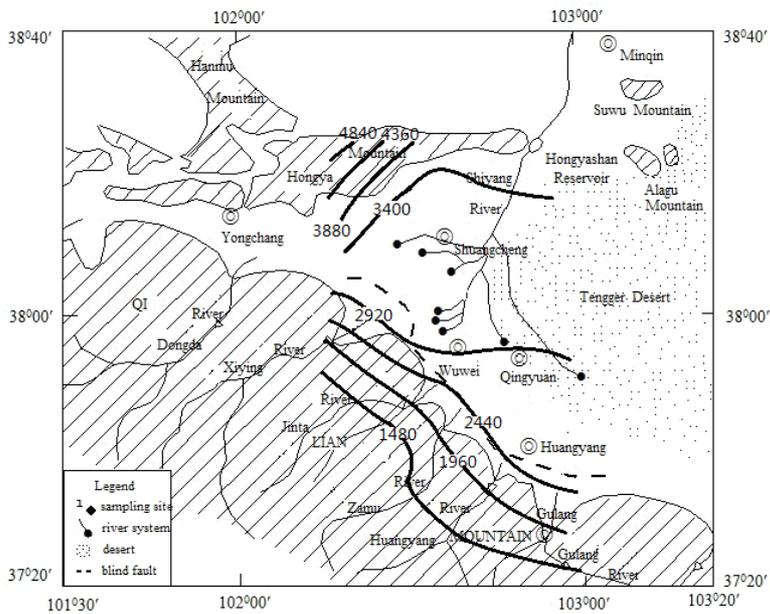


Fig. 5: Carbon-14 age distribution of confined water in the study area.

tem steady flow concentration parameter when the information transmission relationships of the groundwater system conform to the linear rule, and the change of the groundwater flow velocity is negligible compared with the average residence time of groundwater. The tritium input and output concentration relationship in the groundwater system:

$$C_{out}(t) = \int_0^{\infty} C_{in}(t-t')g(t')e^{-\lambda t'} dt' \quad \dots(2)$$

Where,  $t$ - sampling time (s);  $t'$ - tritium migration time (a);  $\lambda$ - tritium decay parameter;  $C_{out}(t)$ - output tritium concentration function;  $C_{in}(t-t')$ - concentration of tritium input function

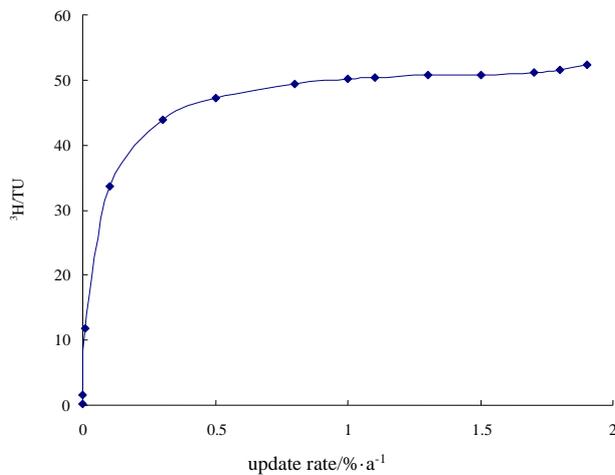


Fig. 6: The related curve update rate and <sup>3</sup>H concentration of groundwater.

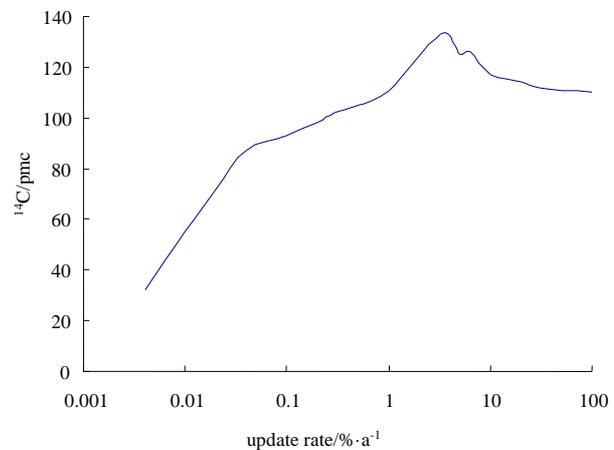


Fig. 7: The related curve update rate and <sup>14</sup>C concentration of groundwater.

tion;  $g(t')$ - groundwater age distribution function. According to the geological condition in the study area,  $g(t')$  was calculated using the index-piston flow combination model (EPM):

$$g(t') = \begin{cases} (\eta/t_i) \exp(-\eta t'/t_i + \eta - 1), & t' \geq (1-\eta^{-1})t_i \\ 0, & t' < (1-\eta^{-1})t_i \end{cases} \dots(3)$$

The relationship between the output concentration and age was calculated using formulas (2) and (3). Then, the groundwater age of sampling points was obtained using the wiring method (Table 1).

In this case, the groundwater was very young. The mean residence time of shallow groundwater in the Wuwei Basins was between 47 and 71a. In the piedmont, groundwater recharged fully because the aquifer medium particles are bulky; the groundwater age is between 5-10 years, and the groundwater renewal ability is the strongest. In the piedmont, the groundwater age is 47-58 years due to limited seasonal river supply ability, and the groundwater renewal ability is relatively low. In the fine soil plain, groundwater circulation conditions worsen because of generally large particles and age (> 50 years), and a poor renewal ability.

#### Residence Time Based on <sup>14</sup>C Data

The <sup>14</sup>C with a half-life of approximately 5730a (Clark et al.1997), has been widely used to estimate the residence time of pre-modern groundwater. Derivation of an absolute age for groundwater requires knowledge of the sources and the initial activity of CO<sub>2</sub> in the vadose zone during recharge. However, because the activity of <sup>14</sup>C in carbonate minerals and the stoichiometry of congruent and incongruent reactions along the flow path interact to produce total

dissolved inorganic C (as HCO<sub>3</sub><sup>-</sup>) in groundwater, it is difficult to estimate the initial <sup>14</sup>C activity. A rough estimate of about 80 pmc for the upper limit of the initial <sup>14</sup>C activity of recharging water has been broadly used in northwestern China (Edmunds et al. 2006, Zhu et al. 2008, Ma et al. 2010).

Using this value, the corrected age of the groundwater was calculated (Table 2). The residence time in the Wuwei Basin ranges from modern times to 5.8 ka, which is equivalent to the dates ranging from modern times to the late Pleistocene. The groundwater in the Baiyun and Shiyanzhan is generally young. Two representative samples yielded values of 88.3 and 81.5 pmc, which are higher than the 50 pmc value of modern water (Chen et al. 2006). The confined waters in the Wuwei basins had ages ranging from 1 to 5.8 ka, with <sup>14</sup>C values ranging from 48 pmc to 88 pmc. The deep groundwater in the piedmont of the Hongya Mountains is very old, with one sample well having an age of 5.8 ka.

The deep groundwater in the study area (> 100 m) ranges in age between 1000-5800 a (Fig. 5). The age showed an increasing trend from the piedmont to the rump. Piedmont groundwater mainly accepts piedmont recharge from runoff into infiltrated water; groundwater cycles are relatively positive; therefore, the deep groundwater age is younger. An investigation of groundwater age between 2920-3400a indicated a small variation range. This is mainly because in the central basin, due to mining groundwater irrigation, part of the confined aquifer is damaged, and the water has mixed with infiltrated water. In the rump area, the deep groundwater age is 4000a or older. The water cycle is slow; the recharge of groundwater water is limited, and therefore, the groundwater age is bigger.

Table 1:  $^3\text{H}$  calculated value of groundwater.

Sample no.	Site	Water type	pH	$^3\text{H}$ (TU)	Age (a.BP)
6	Gaogou	groundwater	6.0	2.85	58
7	Yujiawan	groundwater	6.0	0.9	71
9	Baiyun	groundwater	5.5	50.78	47
12	Liuquan	groundwater	6.5	1.49	66
1	QilianMountain	melt water	5.5	35.43	45
13	Caiqi	surface water	6.0	6.76	5

Table 2: Sample point  $^{14}\text{C}$  value.

Sample no.	Site	pH	$^{14}\text{C}$ (pmc)	Age (BP)
4	Shiyangzhan	7.0	81.4996	1645
5	Dawan	6.0	66.9869	3220
6	Gaogou	6.0	74.7928	2335
7	Yujiawan	6.0	72.7173	2560
8	Hongshuihe	6.5	48.5654	5800
9	Baiyun	5.5	88.2733	1000
10	Qijiahu	6.0	62.7277	3745
11	Xigou	6.5	54.2718	4910
12	Liuquan	6.5	56.5280	4580
13	Canqi	6.0	86.0702	1205

Table 3: Renewal rate of unconfined water.

Sample no.	Site	Water type	pH	$^3\text{H}$ (TU)	Renewal rate (%/a)
6	Gaogou	groundwater	6.0	2.85	0.002
7	Yujiawan	groundwater	6.0	0.9	0.0006
9	Baiyun	groundwater	5.5	50.78	1.0
12	Liuquan	groundwater	6.5	1.49	0.001

Table 4: Renewal rate of confined water.

Sample no.	Site	Water type	pH	$^{14}\text{C}$ (pmc)	Renewal rate (%/a)
4	Shiyangzhan	groundwater	7.0	81.4996	0.032
5	Dawan	groundwater	6.0	66.9869	0.017
6	Gaogou	groundwater	6.0	74.7928	0.022
7	Yujiawan	groundwater	6.0	72.7173	0.02
8	Hongshuihe	groundwater	6.5	48.5654	0.0078
9	Baiyun	groundwater	5.5	88.2733	0.045
10	Qijiahu	groundwater	6.0	62.7277	0.013
11	Xigou	groundwater	6.5	54.2718	0.0096
12	Liuquan	groundwater	6.5	56.5280	0.011
13	Caiqi	groundwater	6.0	86.0702	0.038

### Renewal Rate of Groundwater

Determination of the groundwater renewal rate is important for the sustainable development and utilization of groundwater resources. The groundwater renewal rate (R) is a ratio of make-up water volume ( $V_i$ ) and total storage water volume ( $V_j$ ) in the groundwater system. According to the principle of mass balance, using the full hybrid model (IAEA

2001, Le et al. 2001), the renewal rate formula is:

$$A_{gi} = \frac{A_0}{\frac{\lambda}{R} + 1} \quad \dots(4)$$

Atmospheric  $\text{CO}_2$  is relatively uniformly distributed across the Northern and Southern hemispheres (Fontes et al.

1984). Therefore, changes in the  $^{14}\text{C}$  concentration measured in the Northern hemisphere can be used for research in this area. Before 1905, the change in the atmospheric  $^{14}\text{C}$  concentration was not large, generally around 100 pmc (Stuiver et al. 1991). During the period 1905-1950, the concentration of radioactive carbon in the atmosphere decreased slightly due to the burning of fossil fuels, i.e., between 99.5-97.5 pmc (Suess 1971). We adopted an average value of 98.5 pmc in the calculation.  $^{14}\text{C}$  concentrations of atmospheric precipitation are greatly influenced by nuclear explosions from 1953 to 1963. In the Northern hemisphere, the  $^{14}\text{C}$  concentration reached approximately 200 pmc in 1963. We checked the data according to the literature (Vogel 1970). The atmospheric  $^{14}\text{C}$  concentration was checked according to the literature from 1966 to 1985 (Fontes et al. 1984). The atmospheric  $^{14}\text{C}$  concentration was calculated by exponential decay in 1997-2009.

The relationship curve of groundwater isotopic concentrations ( $A_{\text{gr}}$ ) and the annual renewal rate (R) during sampling (2009 year) was obtained according to the model. Then, using the wiring method according to the measured concentration of groundwater, the sampling points can be used to check the renewal rate of the groundwater. The calculation results according to the model are shown in Fig. 6.

The renewal rate of sampling points can be checked using the measured  $^3\text{H}$  values, in the range of 0.0006-1.0 %/a (Table 3). The maximum calculated groundwater output concentration was 50 TU based on the relationship curve, corresponding to the groundwater renewal rate of 1.0 %/a. Some measured tritium concentration in groundwater exceeded 50 TU in the study area. According to the previous analysis, the tritium concentration in groundwater exceeds 50 TU containing nuclear explosions, the tritium is aged between 30-38 years, and theoretically the renewal rate of 0.3-2.6%/a. Therefore, the tritium concentration exceeds 50 TU corresponding to the renewal rate of groundwater value 1.0%, error less than 0.5%/a, is acceptable.

According to the model, we calculated the output of groundwater  $^{14}\text{C}$  concentration in the study area, and obtained the relationship curve of groundwater  $^{14}\text{C}$  output concentration and renewal rate (Fig. 7).

A sample point renewal rate ranging between 0.0078-0.045‰ can be obtained by using the groundwater  $^{14}\text{C}$  concentration (Table 4). The maximum renewal rate was measured in BaiYun Village, which is in the centre of the irrigated area. Therefore, groundwater alternates frequently, with the deep groundwater renewal rate under the influence of irrigation water infiltration. The minimum

value of the renewal rate was measured in the Hongshuihe village, which lies in the north-central region of Wuwei basin. The deep groundwater was formerly the old water supply and rarely the modern water supply.

## CONCLUSIONS

The groundwater recharge rate not only reflects the groundwater system renewal index, but is also an important parameter in the evaluation of groundwater resources. In arid areas, due to spatio-temporal changes and lower recharge, it is difficult to estimate the groundwater recharge rate directly. Thus, the renewal rate is an important index to understand the groundwater renewal ability of arid areas.

The shallow groundwater in the study area was very young. The mean residence time of shallow groundwater in the Wuwei Basins was between 47 and 71 years. In the piedmont, groundwater recharged fully because of the bulky aquifer medium particles; the groundwater age was between 5-10 years, and the groundwater renewal ability was the strongest. In the piedmont, the groundwater age was 47-58 years due to limited seasonal river supply ability, and the groundwater renewal ability was slightly poor. In the fine soil plain, the groundwater circulation conditions were worse due to particles and greater age (> 50 years), and there was a poor renewal ability.

The age of deep groundwater in the study area (> 100 m) ranged between 1000-5800 years (Fig. 5). Age showed an increasing trend from the piedmont to the rump. The Piedmont groundwater mainly accepted piedmont recharge from runoff into infiltrated water; the groundwater cycles were relatively positive; and therefore, the deep groundwater age is younger. The groundwater age was between 2920-3400 years, and the variation range was not large. This is mainly because in the central basin, due to mining groundwater irrigation, part of the confined aquifer is broken-down, and there is mixing with infiltrated water. In the rump area, deep groundwater is aged 4000 years or older. The water cycle is slow; the recharge of groundwater quantity is limited; therefore, the groundwater age is higher.

The renewal rate of sampling points can be checked using the measured  $^3\text{H}$  values, in the range of 0.0006-1.0 %/a. The maximum calculated groundwater output concentration was 50 TU using the relationship curve, corresponding to a groundwater renewal rate of 1.0%/a. Sample point renewal rate ranging between 0.0078-0.045‰ can be obtained by using the groundwater  $^{14}\text{C}$  concentration. The lower  $^{14}\text{C}$  concentration results indicate that the majority of the deep groundwater is principally maintained

by palaeo water rather than modern recharge, and any exploitation would result in it being depleted. Currently, a depression zone is being created around Wuwei city.

## ACKNOWLEDGEMENT

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