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應用穩定氫氧同位素評估地下水資源

APPLICATION OF STABLE HYDROGEN AND OXYGEN ISOTOPES ON GROUNDWATER RESOURCES ASSESSMENT

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摘 要

臺灣因地形及降雨等分佈不均導致區域水文歷程和地面水/地下水交互補注特性有所變化，因此瞭解其交補關係乃為水資源管理重要課題。

本研究藉由現地採樣、氫氧同位素/化學離子示蹤和數理模式，探討濁水溪沖積扇上游山區及扇頂區域雨水、河水與地下水之時空變異關係，並研判地下水補注來源及補注量。根據雨水、河水與地下水同位素/化學離子組成，以及質量平衡法估算地下水補注來源，顯示皆以河水為主；應用天水線及化學離子多變量分析，將補注水源分成山區北區、山區南區及扇頂區域，局部區域地下水有較輕 $\delta^{18}O$ 值，應受濁水溪側向補注和上游山前補注影響；另以穩定基流分析法及 Modflow 模式估算沖積扇上游山區及扇頂區域地下水年補注量分別為 10.95 及 2.49 億噸/年，結合素質量平衡法推估沖積扇上游山區雨水/河水之年補注地下水比例為 25.9 %及 74.1 %、扇頂區域為 37.3%及 62.7%，量化估算上游山區雨水/河水年補注量分別為 2.83 及 8.12 億噸/年、扇頂區域為 0.93 及 1.56 億噸/年。

本研究綜合應用現地採樣及水文定性/定量評估，探討時空地面水/地下水交互補注機制並量化地下水補注量，研究成果可作為擬定地下水資源管理計畫之參考。

關鍵詞：地下水、濁水溪、穩定氫氧同位素、補注機制。

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ABSTRACT

Effective use of limited water resources is often difficult in Taiwan due to the steep topography, rapid steam flows and uneven spatial-temporal distribution of precipitation. In addition, the climate changes alter the precipitation pattern of the local hydrologic condition, which creates significant impacts on the groundwater recharge. Therefore, it is critical to accurately assess the interactive recharge from the upstream mountain blocks to the downstream alluvial fan for groundwater resources management. In-situ measuring of stable oxygen and hydrogen isotopes, chemical ion tracer method and numerical groundwater model were applied to determine the relationship between the spatial-temporal variation in rainfall, river water, and groundwater in the upstream mountain blocks and proximal fan area of the Choushui river and the relative influence mechanisms.

The results showed that the groundwater mainly recharging from river water both in high and low flow periods and more significant in low flow period. Lighter $\delta^{18}O$ discovered in groundwater at certain local regions indicated that recharge sources may come from the lateral recharge of the Choushui river and the upstream mountain blocks. Annual groundwater recharge amount estimated from stable base flow analysis and numerical simulation of Modflow model were 1.095 billion tons/year and 249 million tons/year for the upstream mountain blocks and proximal fan, respectively. Moreover, based on the oxygen isotope material balance result, the percentages of annual groundwater recharge from rainwater and river water in the upstream mountain blocks were 25.9 % and 74.1 %, respectively, and those in the proximal fan area were 37.3 % and 62.7 %, respectively. The quantity of groundwater recharge in the upstream mountain blocks was estimated to be 283 and 812 million tons/year from rainwater and river water, respectively, and that in the proximal fan area was 93 and 156 million tons/year, respectively. The results may serve as a reference for formulating a regional groundwater resources management plan.

Keywords: Groundwater, Choushui river, Stable hydrogen and oxygen isotope, Recharge mechanism.

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1. Introduction

Even though there is high annual precipitation in Taiwan, the steep terrain and the torrential stream still result in the water source being unable to be used effectively. A great assessment and an applicable development of water source seem to be one of the critical environmental issues. Groundwater, compared with surface water, has the characteristic of stable water quality and quantity. Also, groundwater is easy to obtain and low cost, so it gradually becomes a substitute water source in areas lack of surface water source.

The Choushui river alluvial fan, especially in Changhua county and Yunlin county, now face the difficulties of groundwater lever declination and ground subsidence due to the over pumping of groundwater, causing the severe social and economic problems. In order to solve these, the hydrogeological characteristics and the groundwater recharge capability need to be estimated, and once the recharge mechanism and frequency are clearly recognized, the appropriate groundwater usage plan can also be established.

The natural isotopes in hydrological conditions often generate the isotope fractionation because of the physical, chemical, or kinetic effects, and form the various concentration of isotopes in the hydrological cycle. The transition of the water cycle can be elucidated by the isotope concentration differences. Water is composed of oxygen and hydrogen atoms. In a normal condition without phase changes or fractionations, the isotopes in water maintain the constant value, so the stable oxygen and hydrogen isotopes are good natural tracers to observe the hydrological cycle. Also, they are used to observe the seasonal differences and to evaluate the sources of water (Clay *et al.*, 2004). By applying the oxygen isotope material balance analysis, the recharge from leakage of the river bed is about 34 %, and from precipitation is about 22.9 %, and the total 56.9 % in the Choushui River basin is the main groundwater recharge (Chiang *et al.*, 2005).

The oxygen and hydrogen isotopes are distinctly heavier in the irrigation period than in the non-irrigation period, and they show the difference between the seasons. Also, the $\delta^{18}O$ and δD of precipitation would vary regularly depending on the season. In the wet season, the rainfall and the temperature increase so the $\delta^{18}O$ and δD become lighter. In the dry season, the rainfall decrease and the temperature increase so the $\delta^{18}O$ and δD become heavier. The result can further evaluate the difference of the rainfall upon the groundwater recharge. The upstream isotopes are lighter than the downstream isotopes, and this is attributed to the attitude influence (Yuan *et al.*, 2008).

The oxygen and hydrogen isotope results indicate the shallow, middle, and deep groundwater with stratification. The precipitation influences on the groundwater depth is about 40 m. The result can be used to estimate the hydrological and geological characteristic and determine the recharge time (Kao *et al.*, 2007).

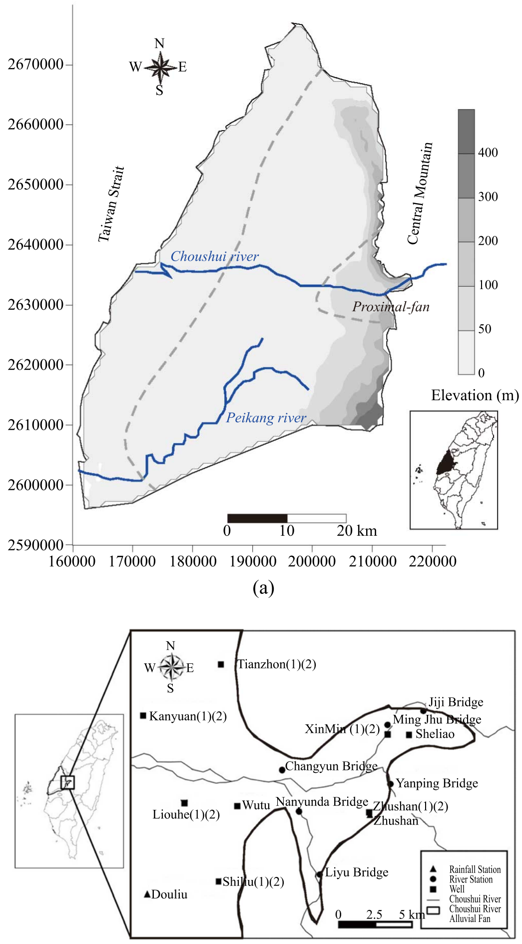
In this study, the stable oxygen and hydrogen isotopes and ions tracer method and numerical models are used to perform the qualitative spatial-temporal analysis in the hydrological identity of the proximal fan of the Choushui River alluvial fan and the upstream mountain blocks, and to estimate the ratio of sources of groundwater recharge.

2. Material and method

2.1 Study area

The study site (Fig. 1) is located in the upstream mountain blocks and the proximal fan of the Choushui River alluvial fan and in Taiwan. The geology of the proximal fan is Tertiary Metamorphic Slate, and it contains the complex folds and faults that usually cause the landslides and wind erosion (Central Geological Survey, 1999). The proximal fan has no distinct aquitards between each aquifer, so the surface water can recharge to the groundwater directly.

On the basis of accelerator mass spectrometry ^{14}C (radiocarbon isotope) dating of mollusk shells in core samples of the Choushui River alluvial fan (Central Geological Survey, 1999), the geologic ages of core samples in the distal fan to the mid-fan could be grouped as follows: 2,931 to 5,364 yr, 7,090 to 9,230 yr, and older than 36,400 yr. Sedimentary formation was in the late Quaternary period and extended to a depth of approximately 300 m (Central Geological Survey, 1999). The shallow aquitard with depths of 0 to −55 m was deposited 3–9 ka ago during the Holocene transgression, the middle aquitard with depths of −100 to −155 m was



(a)

(b)

Fig. 1. (a) The whole area and boundary of the Choushui River alluvial fan. (b) The study site with the rainfall stations, river water stations, and groundwater stations.

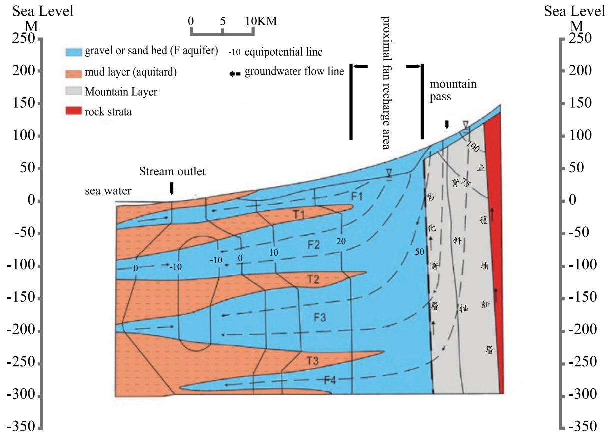


Fig. 2. Conceptual hydrogeological profile of the aquifer system in the Choushui River alluvial fan (modified from Central Geological Survey, 1986).

deposited 35–50 ka ago, and the deep aquitard was deposited 80–120 ka ago. On the basis of subsurface hydrogeological analysis up to a depth of approximately 300 m, the hydrogeological environment is divided into four types of aquifers (Fig. 2): aquifer 1 with depths of 0–103 m, aquifer 2 with depths of 35–217 m (divided into 2-1 and 2-2 with depths of 35–155 m and 100–217 m, respectively), aquifer 3 with depths of 140–275 m, and aquifer 4 with depths exceeding 271 m (Central Geological Survey, available from http://hydro.moeacgs.gov.tw/).

The watershed area of the Choushui River is 3,156.9 km^2 (Water Resources Agency, available from http://www.wra.gov.tw/). The annual average water quality of the Choushui River in 2015 is as follows: pH = 8.33, EC = 506 μmho/cm, DO = 8.58 mg/L, NH_4^+ = 0.13 mg/L, TOC = 1.4 mg/L, NO_3^- = 3.89 mg/L, Mn = 0.482 mg/L, and As = 0.0031 mg/L (Environmental Protection Administration, available from http://www.epa.gov.tw/). The annual precipitation in the Choushui River alluvial fan is 1,972 mm in 2015, mostly concentrated in April to October (rainy season), and the historical yearly rainfall averages 2,366 mm (Water Resources Agency, available from http://gweb.wra.gov.tw/wrhygis/). The main land use of the Choushui River alluvial fan is for agriculture, including rice cropping and upland farming, accounting for 60%, whereas the main land use in the coastal area is for aquaculture (Fig. 3; Environmental Protection Administration, 2014). Recharge sources including rainfall, rivers, boundary inflow, and groundwater irrigation have not been individually accounted for in previous studies. However, Hsu *et. al* (2015) used groundwater storage hydrograph and isotope analysis to estimate the pumpage and recharge of groundwater in the Choushui River alluvial fan, and the result showed that the amount of yearly pumpage for irrigation averaged 1.49 billion ton in 2012 to 2014, whereas that for non-irrigation was 0.867 billion ton. The groundwater level is from 2 m to 55 m, and in most areas of the study site, the groundwater level is < 20 m.

The rainfall, river, groundwater sampling locations were selected within the study site. Two rainfall stations are Yen-Ho junior high school in the upstream mountain blocks and the Douliu Key Telephone System in the proximal fan. Six discharge stations are Jiji Bridge, Ming Jhu Bridge, Yanping Bridge, Liyu Bridge, Nanyunda

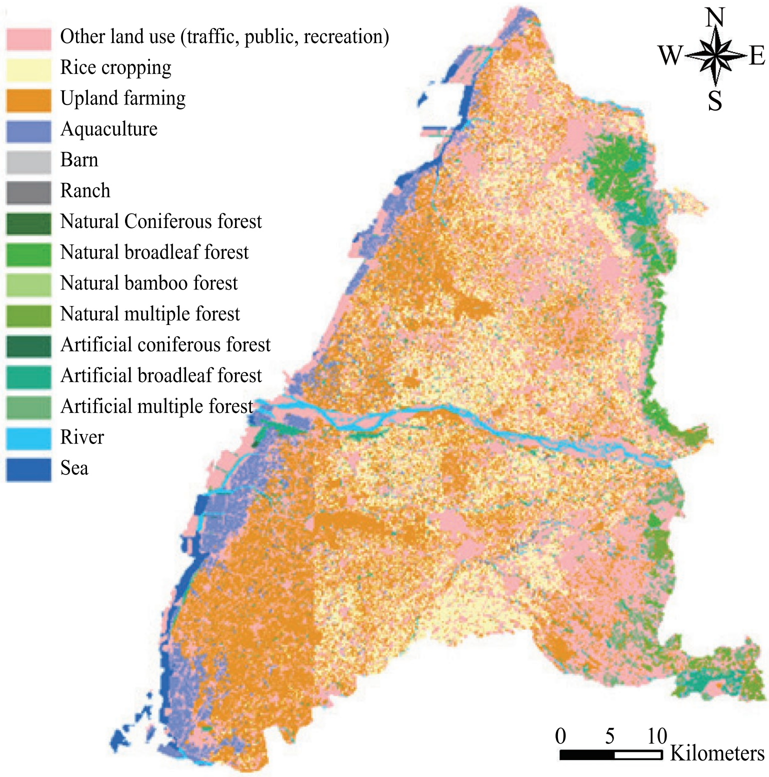


Fig. 3. Schematic for land use in the Choushui River alluvial fan (modified from Environmental Protection Administration, Taiwan, 2014).

Bridge and Changyun Bridge. The groundwater stations from Water Resources Agency are Zhushan (1) (2), Sheliao, XinMin (1) (2) upstream and Tianzhon (1) (2), Kanyuan (1) (2), Shihliu (1) (2), Liouhe (1) (2), and Wutu downstream (Fig. 1). The depth of the most groundwater wells is < 200 m, which belongs to the first and the second aquifer layers.

The precipitation sampling bottles for each rainfall were collected, and then the bottles were sealed tightly for preventing from the evaporation and isotopes fractionation. There are 23 samples of precipitation for each rainfall event.

The shallow flowing river samples excluded the impurities which may influence the quality were collected, and the water quality parameters including pH value, conductivity, dissolved oxygen and redox potential were immediately measured on-site. Then, the samples were sealed in two 1L-bottles, and the nitric acid was added to one of them in order to adjust pH less than 2 and to stabilize the cations. 34 river samples were collected.

Before the samples were collected, the wells should be purged according to the regulation and recorded the in-situ water quality parameters. After the parameters including pH value, conductivity, dissolved oxygen and redox potential were stable, the samples were ready to be collected and sealed in two liter bottles. Then, the nitric acid was added to adjust pH less than 2 and to stabilize the cations. 82 groundwater samples were collected.

In the study area, the long-term discontinuous data were collected and compiled by Wang *et al.* (1998). The $\delta^{18}O$ data of the rainfall in Nantou from 1995 to 2005 were collected. The $\delta^{18}O$ data of the river in Jiji Bridge, Ming Jhu Bridge, Nanyunda Bridge and Changyun Bridge from 1997 to 2001 were also collected. Moreover, the $\delta^{18}O$ long-term data from groundwater station in this study site from 1999 to 2001 were also collected.

2.2 Analytical methods

Hydrologic and geologic characteristics were used to identify the sources and quantity of groundwater recharge as the basis for hydrologic history interpretation. The composition of stable oxygen and hydrogen isotopes, chemical ions sampled from rainwater, river water and

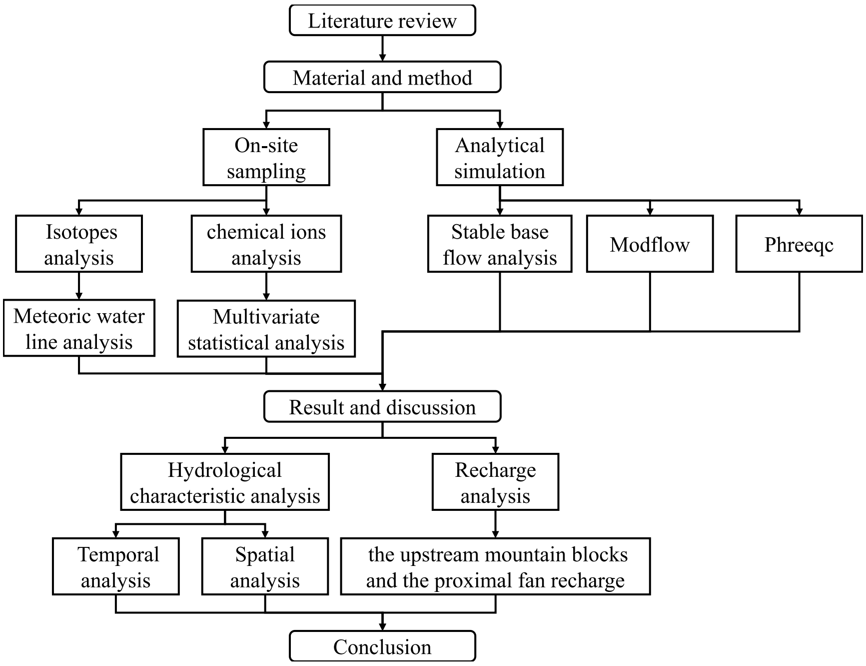


Fig. 4. The conceptual framework of analytical methods of this study.

groundwater in high and low flow periods were also analyzed. The percentage of groundwater recharge sources was estimated using oxygen isotope material balance method.

The sources of groundwater recharge were grouped into the northern upstream mountain blocks, the southern upstream mountain blocks, and the proximal fan, using the meteoric water line for oxygen and hydrogen isotopes and multivariate statistical analysis for chemical ions.

In-situ sampling analysis and qualitative/quantitative evaluation of local hydrology were combined for the investigation on the interactive recharge mechanism between surface water and groundwater in different spatial-temporal settings and for the quantification of regional groundwater recharges.

Overall, the working procedure of this study is illustrated as the flow chart of Fig. 4, which clearly shows the conceptual framework of analytical methods as follows.

2.2.1 Oxygen and hydrogen isotopes analysis

For isotopic analysis of H_2O, the $\delta^{18}O$ and δD values were determined using well-established methods (International Atomic Energy Agency, 1983) on a high precision isotopic water analyzer. The material balance principle was used to analyze the ratio of the water sources. The rainfall, river, groundwater samples were analyzed by Picarro Isotopic Water Liquid Gas Analyzer L2130-i. The accuracy of $\delta^{18}O$ is 0.2 ‰ and the accuracy of δD is 2 ‰. The equations of variation in properties between isotopes are expressed as:

$$\delta D=\frac{(D/H)-(D/H)_{SMOW}}{(D/H)_{SMOW}}\times 1000(‰) \quad ....(1.1)$$

$$\delta^{18}O=\frac{(^{18}O/^{16}O)-(^{18}O/^{16}O)_{SMOW}}{(^{18}O/^{16}O)_{SMOW}}\times 1000(‰) \quad ......(1.2)$$

where H is ${}^{1}_{1}H$ in water, D is ${}^{2}_{1}H$ in water, SMOW is standard mean of ocean water bulletined by International Energy Agency.

The $\delta^{18}O$ and δD values in the rainfall, surface water, ocean, and groundwater are different in nature. The rainfall and river infiltration are the main recharge for groundwater. An equation related to the rainfall variation δ_i, the river variation δ_r, and the groundwater variation δ_g is as:

$$\delta_g=\frac{\delta_i V_i}{(V_i+V_r)}+\frac{\delta_r V_r}{(V_i+V_r)}=\delta_i X+\delta_r(1\text{-}X) \quad ....(2)$$

where Vi is the volume of rainfall, Vr is the volume of the river, X is the ratio of rainfall recharge, 1-X is the ratio of river recharge. δ_i, δ_r, δ_g can be calculated by analysis, and X is the only unknown to be solved.

2.2.2 Meteoric water line analysis

Meteoric water is the water formed in the atmosphere, and falls to the ground through the hydrologic cycle. The meteoric water line is a linear graph with the x-axis of $\delta^{18}O$ and the y-axis of δD, and it can be used to evaluate the regression equation. Then, the distribution of oxygen and hydrogen isotopes can distinguish the water sources, the evolution and the interaction between wall rocks. The characteristics of the regional meteoric water line are diverse because of the influences of topography, climate, and hydrological traits. Global meteoric water line (GMWL) can be formulated as follows (Craig, 1961):

$$\delta D = 8\delta^{18}O + 10 \quad \text{(3)}$$

2.2.3 Water chemistry analysis

In general, besides the hydrogen and oxygen isotopes, other ions can also act as natural tracers and used to assess the hydrological change. The Dionex ICS-900 Ion Chromatography is used to measure the composition of ionic compounds in this study.

2.2.4 Multivariate statistical analysis

The factor and the cluster analysis are mainly adopted for the multivariate statistical analysis, and the tool SPSS Statistics (1998) was used for analyses. The components of ions and the isotopes in the river and groundwater in the rainy and dry season were regarded as variables. The data obtained from the factor analysis were applied by the hierarchical method, to evaluate the spatial-temporal distribution of the hydrogen and oxygen isotopes and ions concentration in the study site.

2.3 Modeling

2.3.1 Stable base flow analysis

The volumes of rainfall, river water, and groundwater are correlated with the recharge of groundwater. In order to develop the application of water sources, to quantify the recharge and decrement of groundwater is crucial. PART numerical Program, a model developed by United States Geological Survey, was adopted to separate the base flow and determine the annual recharge of the groundwater in this study.

2.3.2 Modflow

Unlike the surface water, to observe the flow of groundwater is relatively difficult. The useful solution is to establish the numerical model and then simulate the flow. Among all simulation programs, Modflow can be applied to solve the 1-D, 2-D, and 3-D groundwater problems, and also suitable for the stable/transient state and confined/unconfined aquifers. Moreover, Modflow can solve the groundwater flow equation with different possible properties, boundary conditions, and initial conditions. The groundwater flow model of PMWIN (Processing Modflow for Windows, Chiang and Kinzelbach, 2001) was used to determine the groundwater recharge. The time step is one month, and the tolerance error of simulated and true groundwater lever in each monitoring well and is <2m. The modeling procedure is illustrated as the flow chart of Fig. 5.

2.3.3 Geochemical modeling

PHREEQC, a public software developed by USGS and based on thermodynamic databases, belongs to a sort of geochemical programs and is widely used to perform the calculations and simulations of geochemical reactions and transport processes in natural and polluted water, such as aqueous model, ion exchange, surface complexation, solid solutions, transport modeling, and inverse modeling. The program is based on the equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces. The specific applications are mainly the speciation calculations and reactive transport modeling to obtain SI for calcite in river water and groundwater (Postma *et al.*, 2007); the calculations of speciation, mineral saturation indices (SI), and transfer coefficients for minerals selected in inverse geochemical modeling (Sengupta *et al.*, 2014); the speciation analysis of groundwater samples (Hartland *et al.*, 2015); the equilibration run for ionic concentrations (Mapoma *et al.*, 2016). PHREEQC can also model various 1-D transport processes including diffusion, advection, and dispersion. These processes can be incorporated with equilibrium and chemical kinetic reactions (Parkhurst and Appelo 1999).

PHREEQC Interactive Version 3 was adopted in this study. It is a geochemical modeling computer program (Parkhurst and Appelo, 2013), and used to calculate chemical equilibrium speciation, mineral saturation

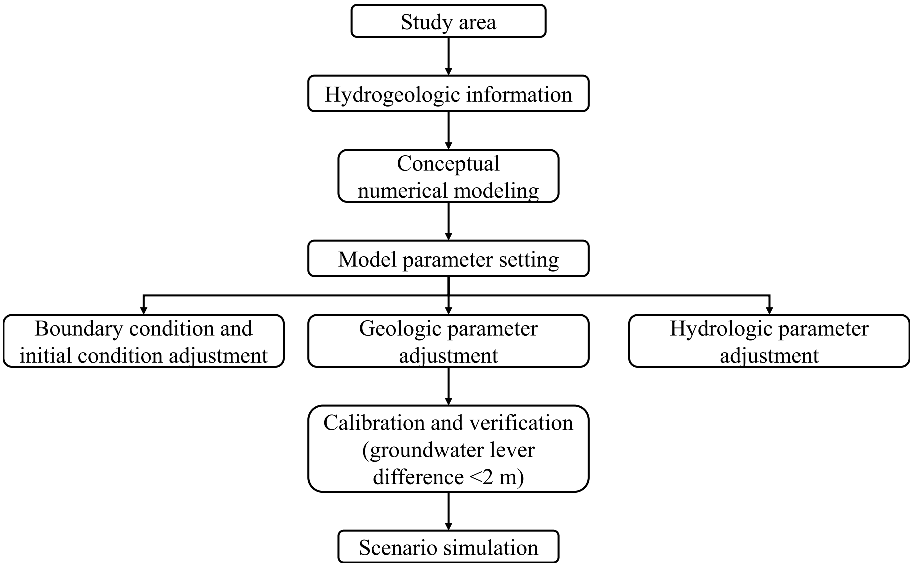


Fig. 5. The modeling procedure of this study.

indices, and to simulate the solutes adsorption of using surface complexation modeling (SCM). The iso.dat database was a partial implementation of the individual component approach for isotope calculations, which is described by Thorstenson and Parkhurst (2002).

3. Results

3.1 Isotopes and chemical ions analysis

The results of hydrogen and oxygen isotope analysis are listed in Table 1 and the average values are plotted in Fig. 6. In the rainfall, the heaviest average $\delta^{18}O$ is −4.23 ‰, and the lightest average $\delta^{18}O$ is −6.27 ‰; the heaviest average δD is −22.39 ‰, and the lightest average δD is −40.42 ‰. The wet season has the relatively low values of $\delta^{18}O$ and δD. In the river, the heaviest average $\delta^{18}O$ is −8.8 ‰, and the lightest average $\delta^{18}O$ is − 11.51 ‰; the heaviest average δD is −57.89 ‰, and the lightest average δD is −81.11 ‰. Compared with the rainfall and the river, the groundwater has the relatively stable values of $\delta^{18}O$ and δD. The heaviest average $\delta^{18}O$ is −8.57 ‰, and the lightest average $\delta^{18}O$ is −9.14 ‰; the heaviest average δD is −58.54 ‰, and the lightest average δD is −61.87 ‰. Fig. 6 indicates that the average values of $\delta^{18}O$ and δD in groundwater are located between those in the rainfall and the river, which is attributed to the mixing effect of isotopes of the rainfall and the river.

Based on the oxygen isotope material balance result, Table 1 shows the ratios of recharge from the rainfall and the river. The river contributes more charges to groundwater, reaching 54.79 % to 79.79 %, while the rainfall contributes less, reaching 29.92 % to 45.21. The recharge ratios of the proximal fan of the Choushui River and the upstream mountain blocks are listed in Table 2. Table 2 shows the same information, which the river contributes more charges, especially in the upstream mountain blocks, reaching 58.9 % to 93.5 %. This may be attribute to a great fluidity in the upstream mountain blocks. The river contributes only 52.5 % to 72.2 % of charges to groundwater in the proximal fan.

Moreover, the result of oxygen isotope material balance suggests the average percentages of annual groundwater recharge from rainwater and river water in the upstream mountain blocks are 25.9 % and 74.1 %, respectively, and those in the proximal fan area are 37.3 % and 62.7 %, respectively (Table 2; Fig. 7a). In other words, 25.9 % of rainfall and 74.1 % of river recharge the upstream mountain blocks, while 37.3 % of rainfall and 62.7 % of river recharge the proximal fan. Fig. 7b suggests that the closest ratios of recharge of the rainfall and the river, both in the upstream mountain blocks and the proximal fan, appear in the wet season of September of 2013.

According to the meteoric water line analysis of $\delta^{18}O$

Table 1. The values of $\delta^{18}O$ and δD in the rainfall, river, and groundwater and the evaluation of the ratio of recharge.

Rainfall				
Year	Season	$\delta^{18}O$ (‰)	δD (‰)	Sample number (n)
1997-2013	Dry Season	−4.23	−22.39	96
	Wet Season	−6.27	−40.42	126
	Average	−5.25	−31.41	–
River				
Year	Month	$\delta^{18}O$ (‰)	δD (‰)	Sample number (n)
2012-2013	Oct-12	−11.11	−77.33	1
	Dec-12	−11.01	−76.62	1
	Mar-13	−10.25	−70.69	1
	Jul-13	−8.8	−57.89	1
	Aug-13	−10.57	−72.66	1
	Sep-13	−11.51	−81.11	1
	Average	−10.54	−72.72	–
Groundwater				
Year	Month	$\delta^{18}O$ (‰)	δD (‰)	Sample number (n)
2012-2013	Oct-12	−9.05	−61.87	13
	Dec-12	−8.57	−58.54	14
	Mar-13	−9.03	−60.59	14
	Jul-13	−9.05	−60.64	13
	Aug-13	−8.83	−59.79	14
	Sep-13	−9.14	−61.87	14
	Average	−8.95	−60.55	–
Ratio of Recharge				
Year	Month	Rainfall (1-X) (%)	River (X) (%)	Sample number (n)
2012-2013	Oct-12	29.92	70.08	13
	Dec-12	36.01	63.99	14
	Mar-13	20.21	79.79	14
	Aug-13	40.49	59.51	14
	Sep-13	45.21	54.79	14
	Average	34.37	65.63	–

Table 2. The ratios of recharge in the upstream mountain blacks and proximal fan.

Area	source	2012-10	2012-12	2013-03	2013-08	2013-09	Average
The upstream mountain blocks	Rainfall (%)	20.6	23.6	6.5	37.5	41.1	25.9
	River (%)	79.4	76.4	93.5	62.5	58.9	74.1
The proximal fan	Rainfall (%)	34.1	35	27.8	42.2	47.5	37.3
	River (%)	65.9	65	72.2	57.8	52.5	62.7

and δD, the study area from light to heavy $\delta^{18}O$ and δD can be sequentially classified into the northern mountain blocks, the northern proximal fan, the southern proximal fan, and the southern mountain blocks (Fig. 8). Reflecting these four classifications to the spatial distribution regions, the regional traits of groundwater and the location of each well on the meteoric water line can also divide the study area into four zones. The spatial distribution of four zones is shown in Fig. 9. The Zone 1 and Zone 2 (the north of Choushui River) have relatively lighter $\delta^{18}O$ and δD than Zone 3 and Zone 4 (the south of Choushui River), indicating the regional traits of groundwater and the sources of recharge may be different.

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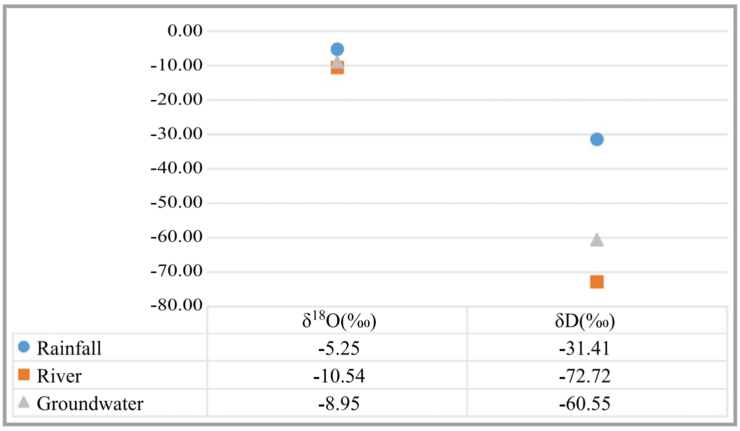
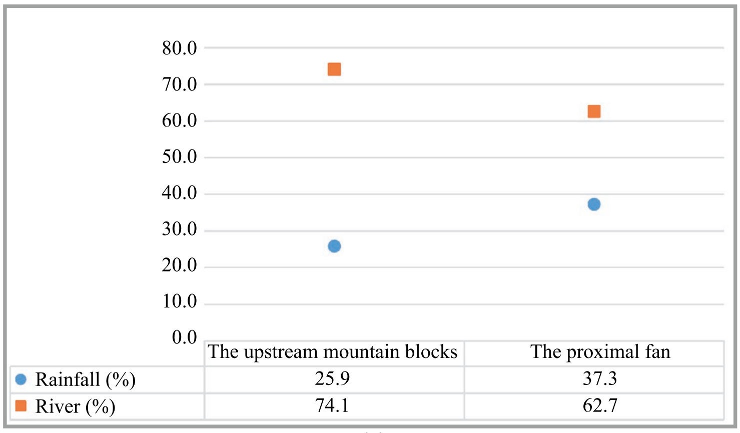


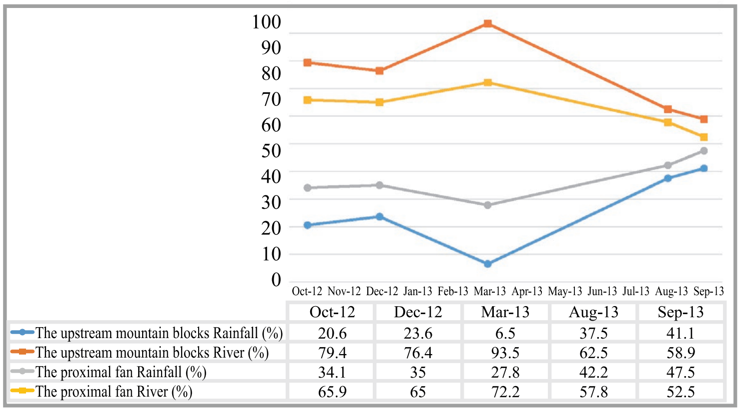
	$\delta^{18}O$(‰)	δD(‰)
Rainfall	-5.25	-31.41
River	-10.54	-72.72
Groundwater	-8.95	-60.55

Fig. 6. The average values of $\delta^{18}O$ and δD in the rainfall, river, and groundwater.



	The upstream mountain blocks	The proximal fan
Rainfall (%)	25.9	37.3
River (%)	74.1	62.7

(a)



	Oct-12	Dec-12	Mar-13	Aug-13	Sep-13
The upstream mountain blocks Rainfall (%)	20.6	23.6	6.5	37.5	41.1
The upstream mountain blocks River (%)	79.4	76.4	93.5	62.5	58.9
The proximal fan Rainfall (%)	34.1	35	27.8	42.2	47.5
The proximal fan River (%)	65.9	65	72.2	57.8	52.5

(b)

Fig. 7. (a) The average ratios of recharge in the upstream mountain blacks and proximal fan. (b) The month ratios of recharge in the upstream mountain blacks and proximal fan.

Seven ion parameters of Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+} were added to perform the factor analysis and cluster analysis by SPSS. The multivariate statistical analysis result shows the study site can be divided into three groups by regional traits, named as Zone 1, Zone 2, and Zone 3. The division is similar to the result of the meteoric water line, but simply from four to three distinct zones.

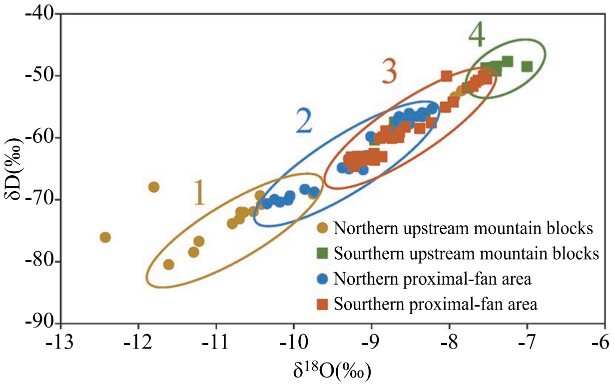


Fig. 8. The division zone of meteoric water line.

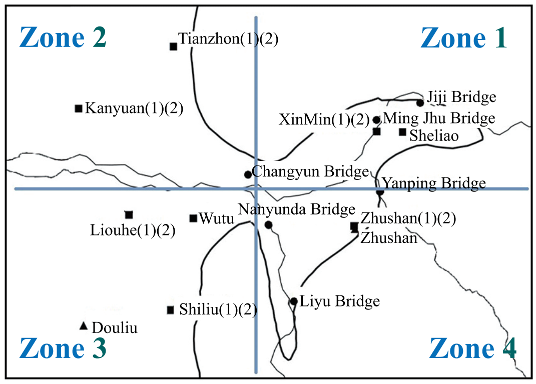


Fig. 9. The spatial four zones divided by meteoric water line.

Table 3. The comparison with experimental data and Phreeqc mixing simulation.

Year	Month	Groundwater sampling		Groundwater Phreeqc_Mixing	
		$\delta^{18}O$ (‰)	δD (‰)	$\delta^{18}O$ (‰)	δD (‰)
2012-2013	2012-10	−9.05	−61.87	−9.052	−60.892
	2012-12	−8.57	−58.54	−8.569	−57.092
	2013-03	−9.03	−60.59	−9.033	−60.929
	2013-07	−9.05	−60.64	-	-
	2013-08	−8.83	−59.79	−8.829	−59.606
	2013-09	−9.14	−61.87	−9.141	−62.714

The following equation is used to discuss the relativity of the value N:

$$N = \frac{C - C_{min}}{C_{max} - C_{min}} \quad \text{.......} (4)$$

where C is the absolute concentration of a single parameter in samples, C_{min} is the minimum concentration of a single parameter within all data, C_{max} is the maximum concentration of a single parameter within all data. N is the relative concentration after normalization. The range of N value is from 0 to 1.

Notably, the normalized groundwater concentrations of stations of Shihliu (1)(2) and Kanyuan (2) were distinctive, which may be influenced by the other water sources.

3.2 Analytical and numerical simulation

PART program was used to calculate the quantity of the base flow in the Yufeng Bridge and the Changyun Bridge. The result of stable base flow analysis shows that the base flow index of the Yufeng Bridge is 62.7 % and the Changyun Bridge is 47.6 %. The groundwater recharge per year from the base flow analysis shows that the Yufeng Bridge is 44.73 cm and the Changyun Bridge is 19.37 cm. Furthermore, the recharge in the upstream mountain blocks is 1,095 million tons/year. The result is close to the previous study of 978 million tons/year by Lee and Chen (2011).

The groundwater flow model is referred from Jang (2003), and numerical simulation of PMWIN is referred from Hsu (2010). The Modflow result shows that the amount of recharge in the proximal fan of the Choushui River alluvial fan is estimated to be 249 million tons/year. Lee (2000) estimated the groundwater recharge using the one-dimensional unsaturated zone long-term hydrological model was 213 million tons in 1995 and 304 million tons in 1996. The above results are similar to our study.

The geochemical modeling (mixing simulation) results of $\delta^{18}O$ and δD in groundwater samples by Phreeqc are listed in Table 3. The results are similar to the laboratory analysis results of $\delta^{18}O$ and δD in groundwater samples. The influence by evaporation was significant in July, and yielded a high ratio of the river recharge.

4. Discussion

4.1 Time sequence analysis

In August of the maximum rainfall period, the $\delta^{18}O$ in the rainfall was the lightest. This suggests that the different precipitation types may influence the composition of rainfall isotopes. In contrast, The $\delta^{18}O$ in the rainfall of the dry season was heavier than the previous compiled data.

Both the $\delta^{18}O$ data in the river and the groundwater had a trend of being lighter than the previous study, especially in the dry season. Both the $\delta^{18}O$ values in the mainstream and the upstream of the the Choushui river are −11.3 ‰ (Central Geological Survey, 2011), which are relatively light, implying that the recharge source in the study site may be influenced significantly by the river water.

The application of the stable hydrogen and oxygen isotope tracer can help to observe the seasonal change in the hydrological cycle and the specific hydrological message from the particular climate. Among them, the $\delta^{18}O$ in the rain water might be influenced easily by precipitation type, followed by the river water, and the $\delta^{18}O$ in the groundwater is the most stable.

Regardless in the wet season or the dry season, the main recharge source in the study site is from the river, especially in the upstream mountain blocks. The result suggests that the surface water and the groundwater interact rapidly due to a great fluidity of geologic condition.

4.2 Spatial distribution analysis

The multivariate analysis result of the study indicates that the region can be divided into three groups: Zone 1, Zone 2, and Zone 3. (Fig. 10)

In Zone 1, the concentration of ions in the surface water changes because of the seasonal variation. Zone 1, the main area of the Choushui river, has high concentrations of Mg^{2+}, Ca^{2+}, SO_4^{2-} and low concentrations of Na^+, NO_3^-, Cl^- in the dry season, which may be attributed to the oxidization of rocks by surface water and the increase of the carbonate concentrations. In contrast, the concentrations of ions are obviously low in the surface water (the river) in

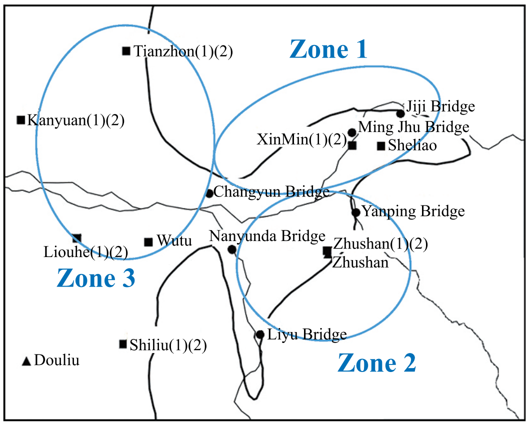


Fig. 10. Three divided zones from regional analysis.

the wet season, which may be caused by the influence of the dilution by rain water.

According to the multivariate analysis result of the groundwater in Zone 2 and the Central Geological Survey (1999), the means of hydrogen and oxygen isotopes are heavier and different from the mainstream where the composition of isotopes is lighter.

The hydrological traits in Zone 3 are similar to Zone 1, and influenced by mineral dissolution. Furthermore, the NO_3^- concentration decreases from the shallow to deep depth. Zone 3 has intensive agricultural activity and is densely populated, which may be influenced by human activity and agriculture practice.

Moreover, the result also suggests that the hydrological pathway of the upstream mountain blocks and the proximal fan (the rainfall of the northern upstream mountain blocks → the mainstream of the Choushui river → the groundwater of the northern proximal fan) is significantly influenced by the focused near-surface recharge (Wilson and Guan, 2004).

4.3 Groundwater recharge analysis

The mean recharge ratios of the rainfall and the river and in the proximal fan are 37.3 % and 62.7, respectively (Table 2), which the ratio of the river is 25 % higher than the rainfall. The mean recharge ratios of the rainfall and the river in the upstream mountain blocks are 25.9 % and 74.1, respectively (Table 2), which the ratio of the river is even 45 % higher than the rainfall. This suggests that the exchange between the river and the groundwater is more rapid than that between the rainfall and the groundwater,

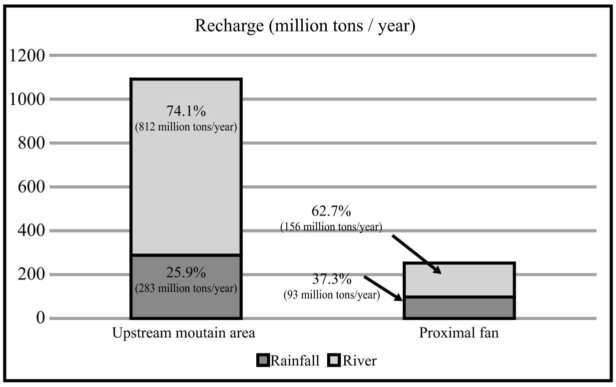


Fig. 11. The recharge proportion of the upstream mountain blocks and the proximal fan.

which may attributed to the high hydraulic conductivity of geological formation.

The recharge sources of the proximal fan identified by this study are similar to the previous study of Hsu *et al.* (2011) who used the groundwater hydrograph and the isotopes tracer analysis to recognize the recharge sources.

The aforesaid ratios between the river and the groundwater can be quantified, and the result indicates that the groundwater recharge in the upstream mountain blocks is 283 million tons/year from the rainfall and 812 million tons/year from the river. Moreover, the groundwater recharge in the proximal fan is 93 million tons/year from the rainfall and 156 million tons/year from the river (Fig. 11).

5. Conclusion

The data of precipitation, river and groundwater samples in the dry and wet season in the proximal fan of the Choushui River alluvial fan and the upstream mountain blocks were collected. The stable oxygen and hydrogen isotopes were applied to evaluate time sequence characteristic and the ratio of groundwater recharge. Moreover, the meteoric water line analysis and multivariate statistical analysis were adopted to analyze the spatial distribution characteristic. The ratio of groundwater recharge was used to evaluate different contribution portions in the proximal fan (Modflow) and the upstream mountain blocks (stable base flow analysis). The mixing simulation (Phreeqc) was used to verify the $\delta^{18}O$ and δD values with the experimental data.

The $\delta^{18}O$ and δD seasonal analysis results suggest that the $\delta^{18}O$ in the rainfall has a wide distribution range and the highest variability, followed by the river water, and the of $\delta^{18}O$ in the groundwater has the most stable distribution range. Although the result is the typical distribution characteristic of oxygen and hydrogen isotopes, it can provide for the information of the spatial-temporal groundwater recharge.

The isotope material balance result of the recharge ratio indicates that the main recharge source in the wet and dry season is the river water in both the upstream mountain blocks and the proximal fan, especially in the upstream mountain blocks. This suggests that due to the distinct geological conditions, the great fluidity results in a rapid interaction between the surface water and the groundwater.

According to the meteoric water line, the wet season is distinctly lighter than the dry season. The study site can be divided into four regions: the northern mountain blocks, the northern proximal fan, the southern proximal fan, the southern mountain blocks. This suggests that the groundwater has specific regional characteristic.

The multivariate statistical analysis (the factor and the cluster analysis) result shows the study site can be divided into three groups by regional traits as follows: (1) Zone 1; the northern upstream mountain blocks, which belong to the mainstream of the Choushui river, and have the lighter composition of oxygen and hydrogen isotopes. (2) Zone 2; the southern upstream mountain blocks, which belong to the tributary of the Choushui river, and have the heavier composition of oxygen and hydrogen isotopes. (3) Zone 3; the northern and the southern proximal fan, which has the values of oxygen and hydrogen isotopes between Zone 1 and Zone 2. Also, the result indicates that Zone 1, Zone 2, and Zone 3 have unlike regional traits, resulting in the sources of recharge being different.

By the stable base flow analysis, the recharge in the upstream mountain blocks is 1,095 million tons/year, and the result corresponds well to the previous study of Lee and Chen (2011). By the Modflow model, the recharge in the proximal fan of the Choushui River alluvial fan is estimated to be 249 million tons/year, which is similar to Lee (2000) using the one-dimensional unsaturated zone long-term hydrological model with 213 million tons/year.

The recharge of the upstream mountain blocks is 74.1 % from the river and 25.9 % from the rainfall. In the proximal fan, the recharge is 62.7 % from the river and 37.3 % from the rainfall. The groundwater recharge is mainly form the river. The results of recharge from the rainfall and river are 283 and 812 million tons/year respectively in the upstream mountain blocks, and are 93 and 156 million tons/year respectively in the proximal fan. The results are useful to formulate a solid groundwater resources management plan. For example, in order to increase the detention time of river water and also increase the recharge volume of the groundwater in the Choushui river alluvial fan, a water storage facility can be considered to be built in the dry season.

Moreover, the hydrological pathway of the upstream mountain blocks and the proximal fan (the rainfall of the northern upstream mountain blocks → the mainstream of the Choushui river → the groundwater of the northern proximal fan) is significantly influenced by the focused near-surface recharge, which may be a reference for the groundwater recharge planning and water storage facility setting.

For future study, the proposed directions are summed as follows: (1) to collect the continuous water samples (including the rainfall, the river water, and the groundwater) for at least 1 to 3 weeks while encountering typhoons or any weather changes. This can avoid missing special messages or important information. (2) to combine the Choushui river alluvial fan and the upstream mountain blocks to be one model (pattern) for simulation, and use the lastest groundwater level data to verify the model. This can decrease the errors in groundwater recharge estimation.

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