



Influence of Evaporation on the Hydrogen and Oxygen Stable Isotopes in an Enclosed Water Body: A Case Study

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ABSTRACT

It is of great significance to study the influence of evaporation on the protection and management of regional water resources. In this study, water samples have been collected from a typical enclosed water body, Liuxi, a small brook in the campus of Suzhou University in May and June, and then analyzed for their hydrogen and oxygen stable isotopes. The results indicate that the samples collected in June have higher $\delta^{18}\text{O}$ and δD values relative to the samples collected in May, and both of them have $\delta^{18}\text{O}$ and δD values plotted at the right of the meteoric line, in combination with their lower deuterium excess (d-excess) values relative to the meteoric line, implying that the water has been influenced by evaporation. Moreover, the d-excess values showed decreasing and increasing in different sampling sites, which was demonstrated to be influenced by different extents of evaporation. Based on the calculation, the residual water quantities were 70–75% and 51–70% for May and June relative to the initial water, which indicates that about 10% of the water had evaporated during May and June.

INTRODUCTION

Surface water is not only the main component of natural water resources, but also an important source for sustaining human life. Compared to the groundwater, surface water is not only the most basic water resource for agriculture, industry and human lives, but also an important resource for natural landscape and entertainment. Surface water is extremely vulnerable to the impact and pollution of the external environment, (Xu et al. 2016). Therefore, a large number of studies related to the surface water environment, quantity, quality and other related issues have been carried out in recent years (Zhang et al. 1997, Xu 2005, Joshi & Seth 2011, Fan et al. 2017, Gao et al. 2018, Wu et al. 2018).

At present, scholars have conducted a great deal of research on the hydraulic connection between surface water and groundwater, the evolution of surface water in the process of precipitation, evaporation and runoff, and the treatment and restoration of surface water environment by using hydrogeochemistry and isotope technology (Buttle 1994, Wang et al. 2018, Xia et al. 2019). In these studies, hydrogen and oxygen stable isotopes, play an important role in the hydrological cycle and water balance calculation, as good tracers (Jiang et al. 2000, Zhang et al. 2006, Zhang et al. 2020).

Suzhou city is located on the Huaibei plain. It is an important industrial and agricultural city in China. Although

there are only small lakes and rivers in Suzhou, they are still very important for urban development and have played an important role in the beautifying of the environment. However, because of their special characteristics, e.g. strong sealing, poor water mobility, small water environment capacity and low self-purification capacity (Zhao 2019), these small lakes and rivers can be easily influenced by human activities.

There were some studies that were carried out for the water bodies in Suzhou city. Most of these focused on the assessment and source approximation of pollutants (Li et al. 2015, Zhang et al. 2018), but there is no report related to their stable isotopes, which is considered to be important for the study of regional water cycle. Therefore, in this study, water samples have been collected from a typical enclosed water body, Liuxi, a small brook in the campus of Suzhou University in May and June, and then analyzed for hydrogen and oxygen stable isotopes. The goals of the study include: (1) obtaining information regarding the compositions of hydrogen and oxygen stable isotopes of the water; (2) finding out the main influencing factors; (3) calculating the degree of influence of evaporation. This brook was chosen because of its relatively closed characteristics and the fact that no rainfall occurred during the two sampling periods, hence, the influence of evaporation can be better obtained. The study can provide the basis for water resources protection and management of regional closed water bodies.

MATERIALS AND METHODS

Study Area

Suzhou city is located in the north of Anhui province, China. It is at the northern gate of Anhui province between longitude $116^{\circ}09'$ - $118^{\circ}10'$ E and latitude $33^{\circ}18'$ - $34^{\circ}38'$ N, with a total area of 9787 square kilometers. The rainfall is concentrated between the middle of July to the beginning of August every year, and may cause floods. The average annual rainfall is 840 mm, and the rainfall is mainly concentrated in summer, fulfilling 50%-60% of the total annual rainfall.

The Liuxi brook is located in the middle of the East Campus of Suzhou University, with a total length of about 500m, a depth of one to one and a half meters, and a width of about ten meters. Because of the dams built on either side of the brook, it is an enclosed water body in the absence of atmospheric precipitation and artificial water supplement, and the loss of water in it is mainly influenced by evaporation.

Sampling and Analyses

According to the hydrogeological conditions of the Liuxi brook, a total of 20 samples were collected on May 5 and

June 5, 2019 (10 samples each time, the specific location and number are shown in Fig. 1). There was no rainfall or artificial water supplement during the period. The samples were collected in was recorded during sampling.

After collection, all of the samples were filtered by a $0.45\ \mu\text{m}$ microporous filter membrane, and the stable hydrogen and oxygen isotopes were measured by liquid isotope analyzer (LGR iwa-45ep). The accuracy shown is $\delta\text{D}<0.5\text{‰}$, $\delta^{18}\text{O}<0.1\text{‰}$, respectively. The results were then calculated with Vienna Standard Mean Ocean Water (VSMOW) standard. The analyzing quality is controlled by the standard sample, and the relative standard deviation is within five percent. All of the measurements were processed in the Key Laboratory of Mine Water Resource Utilization of Anhui Higher Education Institute.

Calculation Methods

The global meteoric water line (GMWL) has been established by (Craig 1961) based on the global atmospheric precipitation isotopic data. Because of the differences of geographical factors and meteorological conditions in different regions, the meteoric water line is different in different regions. At

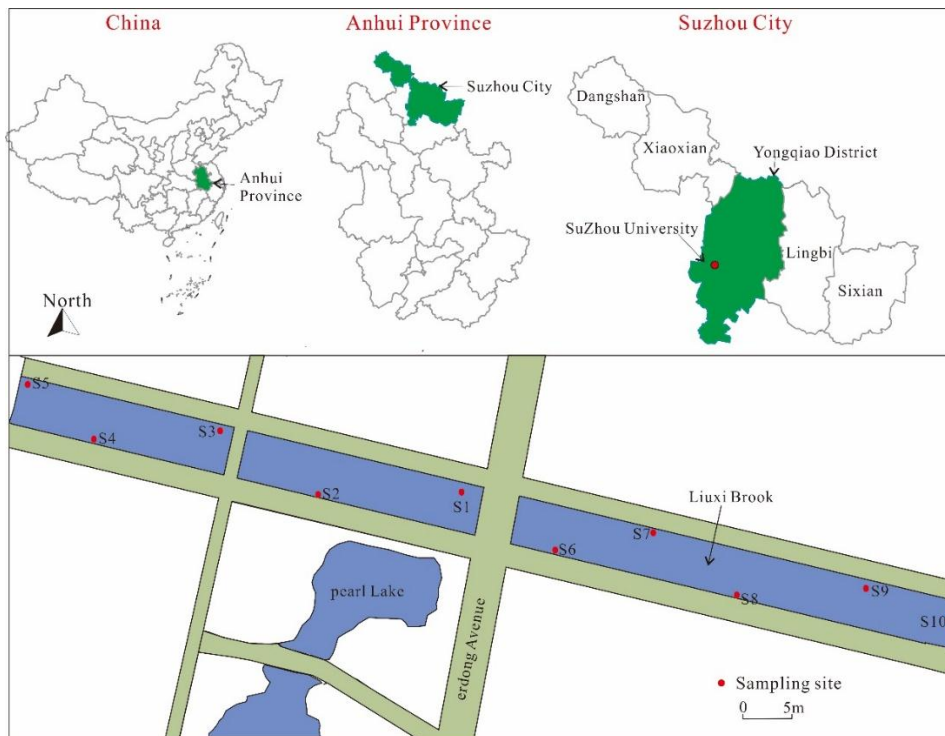


Fig. 1: Location of the study area and sampling sites.

present, due to the lack of precipitation data in Suzhou, the national meteoric water line of China (CMWL) was adopted in this study, and the equation is as follow:

$$\delta D = 7.89\delta^{18}O + 8.16 \quad \dots(1)$$

The evaporation line is a linear regression line between δD and $\delta^{18}O$ of the surface water in a region, and the deviation of the line relative to the meteoric line is a reflection of the degree of evaporation of the region, which varies in different areas. In this study, the evaporation line (MEL) (Chen et al. 2008) in the Huaihe River region have been chosen for comparison, and the equation is as follow:

$$\delta D = 5.89\delta^{18}O - 7.68 \quad \dots(2)$$

Isotopic fractionation refers to the fractionation of light and heavy isotopes in the evaporation process. Because the bonds of the relatively light isotopes are easier to destroy and remove from the water, while the heavy ones remain to enrich the residual water. The isotopic fractionation of water with Rayleigh equilibrium is mainly affected by temperature under evaporation, and its isotopic composition increases exponentially with the decrease of volume ratio of residual water (Shi et al. 2003, Philip 2019). The stable isotope value δ_0 in the initial water body has the following relationship with the stable isotope value δ in the remaining water body:

$$\delta = (\delta_0 + 1)f^{(a-1)} - 1 \quad \dots(3)$$

In the equation, a is the fractionation coefficient, f is the ratio of the residual water. Because the absolute value of δ is small, then the equation (3) can be simplified to be:

$$\delta - \delta_0 = -10^3(a-1)\ln f \quad \dots(4)$$

The fractionation coefficient a is a function of temperature and their relationships are as follows:

Table 1: Results of stable isotope analysis of hydrogen and oxygen in Liuxi water

Sample ID	May			June		
	$\delta^{18}O/‰$	$\delta D/‰$	d-excess	$\delta^{18}O/‰$	$\delta D/‰$	d-excess
S1	-4.90	-38.88	0.35	-4.67	-30.25	7.11
S2	-4.68	-38.66	-1.25	-4.24	-30.97	2.92
S3	-4.60	-39.10	-2.33	-2.26	-38.18	-20.10
S4	-4.67	-38.80	-1.48	-2.60	-36.25	-15.48
S5	-4.66	-38.55	-1.23	-3.33	-32.74	-6.14
S6	-4.58	-38.71	-2.06	-3.61	-30.97	-2.06
S7	-4.72	-37.72	0.03	-3.02	-30.87	-6.68
S8	-4.68	-37.83	-0.39	-3.45	-30.49	-2.87
S9	-4.63	-38.26	-1.23	-4.56	-25.72	10.74
S10	-5.26	-36.62	5.43	-1.74	-39.66	-25.72

$$10^3 \ln a^{18}O = 1.137(10^6/T^2) - 0.4156(10^3/T) - 2.0667 \quad \dots(5)$$

$$10^3 \ln a^D = 24.844(10^6/T^2) - 76.248(10^3/T) + 51.612 \quad \dots(6)$$

RESULTS AND DISCUSSION

Compositions of Hydrogen and Oxygen Isotopes

The hydrogen and oxygen stable isotopes of water samples collected from the Liuxi brook are shown in Table 1. As can be seen from the table, the May samples have δD values range from $-39.10‰$ to $-36.62‰$, with an average of $-38.31‰$, and the $\delta^{18}O$ values range from $-5.26‰$ to $-4.58‰$, with an average of $-4.74‰$. Comparatively, the June samples show higher values of δD and $\delta^{18}O$, the δD are from $-38.18‰$ to $-25.72‰$ (mean is $-32.61‰$), and the $\delta^{18}O$ are from $-4.67‰$ to $-2.26‰$ (mean is $-3.35‰$). Except for the sample S10 in June, the $\delta^{18}O$ and δD values of other samples increased with different extents from May to June, which indicates the influence of evaporation (Tian et al. 2000, Kim et al. 2011). Moreover, in combination with the meteoric line and evaporation line in Fig. 2, except for the sample S9, all the samples are plotted below the meteoric line but near the evaporation line, which further demonstrates that the water in the Liuxi brook has been influenced by evaporation.

Analysis of d-excess

The relationship between δD and $\delta^{18}O$ in different regions tends to deviate from the global meteoric line. This difference was quantified as deuterium excess (d-excess) (Dansgaard 1964), and the equation for it is $d\text{-excess} = \delta D - 8 \times \delta^{18}O$. For the water samples from the Liuxi brook, the d-excess values of samples in May range from $-2.33‰$ to $5.43‰$, with an average of $0.42‰$ (Table 1), whereas the d-excess values of samples in June are from $-20.10‰$ to $10.74‰$, with an average value of $-5.82‰$. All of the samples except for S9 have lower d-excess values relative to the GMWL (Fig. 3), implying the influence of evaporation,

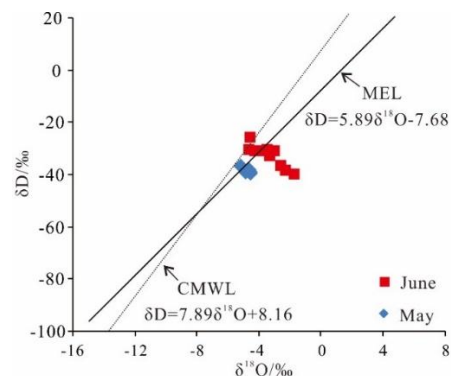


Fig. 2: Relationships between $\delta^{18}O$ and δD .

similar to the results obtained by the comparison of δD and $\delta^{18}O$ in the Fig. 2.

As can be seen from the relationship between d-excess, δD and $\delta^{18}O$ (Fig. 4), the correlation of coefficients between d-excess and δD is 0.865, and is 0.956 between d-excess and $\delta^{18}O$. Both of them are higher than the critical value ($r = 0.765$, $\alpha = 0.01$, $n = 10$), implying that the d-excess values of water samples have been obviously affected by the stable isotope compositions of hydrogen and oxygen. However, it can be obtained from Fig. 3 that the d-excess values of 7 samples decreased while 3 samples increased. During water rock interaction, the $\delta^{18}O$ values in silicate and carbonate rocks are higher than that in water, and the oxygen isotope of the water can be influenced (increasing) during water rock interaction with temperature $> 60^{\circ}C$. Comparatively, the δD values in these rocks is low and cannot influence the hydrogen isotope in water. Under this situation, the d-excess value of the water will decrease (Yao & Lu 2017). However, the water in this study is only $27^{\circ}C (< 60^{\circ}C)$, and therefore, the influence from the water rock interaction can be ruled out.

There are two types of isotopes (1H and 2H) related to the δD , and other two types (^{16}O and ^{18}O) related to the $\delta^{18}O$. Comparatively, the isotopes of hydrogen can be more easily influenced by evaporation relative to the oxygen isotopes because of their different weights. Under the condition of low degree evaporation, the hydrogen isotopes can be more easily fractionated relative to the oxygen isotopes. With the increasing of the degree of evaporation, the differences of fractionation between hydrogen and oxygen isotopes will decrease. Therefore, if the change of δD higher than the change of $8 \times \delta^{18}O$, which means the low degree evaporation, and leading to the increasing of d-excess, alternatively, means the high degree evaporation and leading to the decreasing of d-excess.

From this point of view, although all of the water samples except for the S10 have δD and $\delta^{18}O$ increased, their changing rate are different, which therefore leading to the increasing (S1, 2 and 9) and decreasing (S3, 4, 5, 7, 8 and 10) of the d-excess. From the perspective of change rate, the average change rate of δD between the two month samples is 14.8%, while the average change rate of $\delta^{18}O$ is 29.0%. Therefore, the d-excess values of most samples in June are lower than those in May.

Quantity of Residual Water Relative to Initial Water

The stable isotopic compositions of hydrogen and oxygen in the initial water body is determined by the intersection of local meteoric line and evaporation line, which was calculated to be $\delta^{18}O = -7.92\text{‰}$ and $\delta D = -54.32\text{‰}$ (based on equation (1) and (2)). According to the meteorological data

of the Suzhou, the mean temperature in May and June is $27^{\circ}C (300.15\text{ K})$. The results of the calculations of the proportion of the residual water, relative to initial water based on $\delta^{18}O$ and δD are shown in Table 2 and Fig. 5.

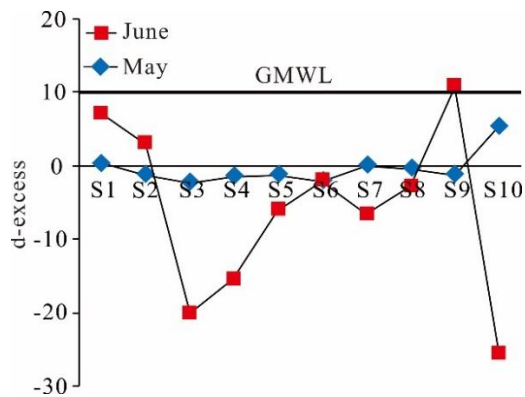


Fig. 3: Variation of the d-excess values.

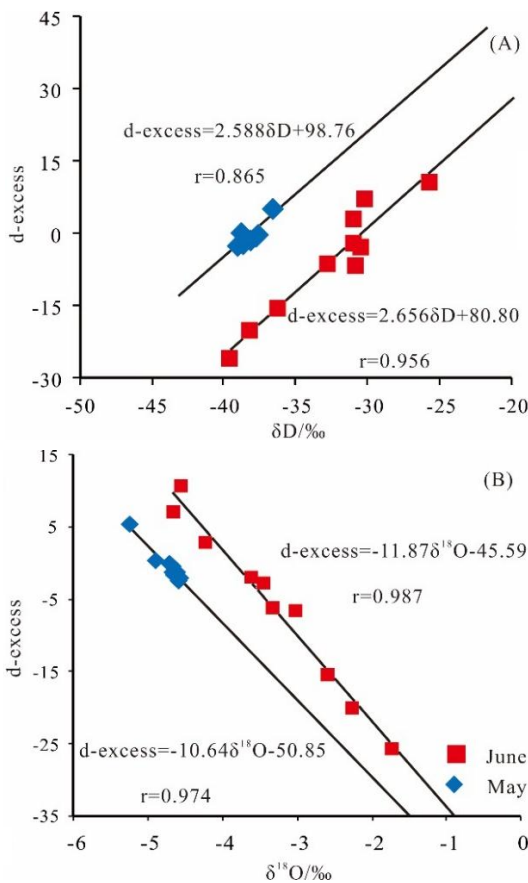


Fig. 4: Relationships between d-excess, δD and $\delta^{18}O$.

As can be seen from the table and figure, based on the values of $\delta^{18}\text{O}$, the proportion of the residual water in May is 70% to 75%. Comparatively, the results are 79%–82% based on the values of δD . As to the June samples, the residual water proportions are 51%–70% for May and 69–82% for June based on the values of δD , respectively. Previous studies revealed that the calculation of the water loss caused by evaporation by using $\delta^{18}\text{O}$ is more accurate, because in the actual situation, water evaporation is also affected by some meteorological conditions such as wind speed and air humidity (Qian et al. 2007). Therefore, the results obtained from the $\delta^{18}\text{O}$ have been accepted in this study. By calculating the proportionate difference of residual water in June and May of each sampling point, the average value of residual water proportion difference calculated by $\delta^{18}\text{O}$ is 10%, which

indicates that the water loss of the Liuxi brook is about 10% and influenced by evaporation from May to June.

CONCLUSIONS

Based on the hydrogen and oxygen isotopes of water samples collected in the Liuxi brook during May and June, the following conclusions have been obtained:

- (1) Most of the samples have higher $\delta^{18}\text{O}$ and δD values in June relative to May, implying that the hydrogen and oxygen isotopes of the water have been influenced by evaporation.
- (2) The influence of evaporation was further confirmed by the lower d-excess values of the water samples relative to the meteoric line. However, the change of d-excess

Table 2: Calculation results of evaporation ratio of each sampling point.

Sample ID	May				June			
	$\delta^{18}\text{O}/\text{‰}$	<i>f</i>	$\delta\text{D}/\text{‰}$	<i>f</i>	$\delta^{18}\text{O}/\text{‰}$	<i>f</i>	$\delta\text{D}/\text{‰}$	<i>f</i>
S1	-4.90	0.72	-38.88	0.82	-4.67	0.70	-30.25	0.73
S2	-4.68	0.70	-38.66	0.81	-4.24	0.67	-30.97	0.74
S3	-4.60	0.70	-39.10	0.82	-2.26	0.54	-38.18	0.81
S4	-4.67	0.70	-38.80	0.82	-2.60	0.56	-36.25	0.79
S5	-4.66	0.70	-38.55	0.81	-3.33	0.61	-32.74	0.75
S6	-4.58	0.70	-38.71	0.81	-3.61	0.63	-30.97	0.74
S7	-4.72	0.71	-37.72	0.80	-3.02	0.59	-30.87	0.73
S8	-4.68	0.70	-37.83	0.81	-3.45	0.62	-30.49	0.73
S9	-4.63	0.70	-38.26	0.81	-4.56	0.69	-25.72	0.69
S10	-5.26	0.75	-36.62	0.79	-1.74	0.51	-39.66	0.82

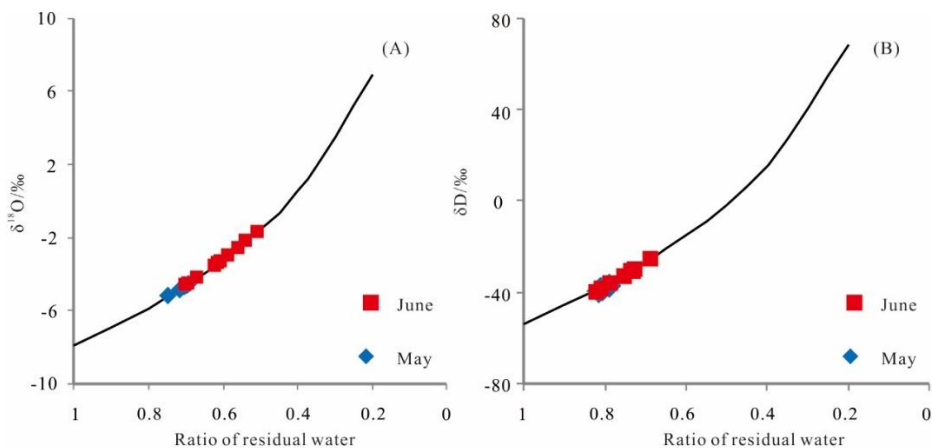


Fig. 5: The relationships between $\delta^{18}\text{O}$, δD and the proportion of residual water.

value has been demonstrated to be influenced by the changing of $\delta^{18}\text{O}$ and δD , which was related to the evaporation.

- (3) According to the calculation based on Rayleigh equilibrium evaporation, the residual water quantities were 70–75% and 51–70% for May and June relative to the initial water, which indicates that about 10% of the water has been evaporated during the period between May and June.

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