

USE OF HYDROGEN AND OXYGEN ISOTOPES TO UNDERSTAND EVAPORATION FROM ENCLOSED WATERBODIES

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Highlights

- ▶ Most samples taken in June have higher δ^{18} O and δ D values than those in May.
- > The variations of d-excess value were controlled by the local environment, e.g., whether the water was shaded or not.
- ▶ The residual water quantities calculated were 53 to 63% and 49 to 56% for May and June, respectively.

Abstract. Getting information on evaporation is important for water resource protection and managing regional enclosed waterbodies. Some lake water samples were collected in May and June from a representative enclosed waterbody – the Pearl Lake, Suzhou, China – and the hydrogen and oxygen isotopes determined. Most samples taken in June have higher $\delta^{18}O$ and δD values than those in May, indicating that there are differences between the intensity of evaporation of May and June. This was further confirmed by the water samples' d-excess values, which were below the meteoric line. However, the variations of d-excess value have been shown to be influenced by source moistures or evaporation processes, which were controlled by the local environment, e.g., whether the water was shaded or not. The residual water quantities calculated were 53 to 63% and 49 to 56% for May and June, respectively, relative to the initial water, indicating that about 5% of the water evaporated between 5 May and 5 June.

Keywords: evaporation, enclosed waterbody, hydrogen and oxygen stable isotopes, Pearl Lake, residual water quantities.

Introduction

Lakes are important surface water bodies, connecting all surface water system elements and forming regional water resources, in other words they have an important role in regional water cycle systems. In addition to providing water resources, lakes are also extremely significant in regional economic and social development. For example, Dongting Lake, Hunan Province, China, is not only an important water resource but also famous land for its fish and rice. Chaohu Lake, Anhui Province, China is an important tourist site as well as providing major regional fishery resources.

Lakes are closely tied to human survival and development, as well as being extremely sensitive to external conditions. A change of water balance or ecological environment will have a serious impact on a lake in general (Huang et al., 2019). Therefore, the key component of current lake research is analyzing changes in the lake's environment, water quantity and quality, and related issues (Liu et al., 2020). Since the beginning of the twentieth century, extensive research has been carried out on lakes, focused mainly on hydrogeology (Caritat et al., 2019; Qi et al., 2015; Ben Yona et al., 2020) and the environment of lakes (Zhan et al., 2016; Emmer et al., 2020; Du et al., 2020; Hartig et al., 2020; Zhuo & Zeng, 2020).

In these studies, isotope, as an important quantitative research method, has played a significant role in the study of lakes with respect to hydrological evolution and environmental assessment (Fang et al., 2017; He et al., 2018; Chen et al., 2019; Gui et al., 2019; Zhang et al., 2019). In isotopes research, stable isotopes also play an important role in studies of lake the tracing the water cycle and assessing the water quality especially such as Gibson et al. (2016), Wu et al. (2017), Biggs et al. (2015).

In northern China, the water-intensive economic development is hindered by severe water shortages for a long

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time (Kattel et al., 2019). Suzhou is an important industrial and agricultural city, typical of Northern Jiangsu and Anhui Provinces, China. In this area, there are some small lakes. They cannot be used for water supply because of their limited quantity but are very important for regional development. For example, the Delta Park built on Delta Lake (an artificial and small lake) in the city, is an important part of the Xinbianhe Water Conservancy Scenic Spot. Previous research has been carried out on surface water in the city but, up to now, the main focus has been on water pollution assessment (Ji et al., 2013; Li et al., 2017).

In this project, Pearl Lake, a typical, small, artificial lake in Suzhou has been used to study the contents of stable isotopes of hydrogen and oxygen at different times, to obtain information about the influence of evaporation on the lake water's isotopic composition. Meanwhile, this study provides further a theoretical basis for regional water environment protection and utilization of water resources.

1. Materials and methods

1.1. Study area

Suzhou is in the north of Anhui Province, China. It is the province's north gate at longitude between E116°09' and 118°10' and latitude between N33°18' and 34°38', and covers 9787 km². The area has semi-humid monsoon – i.e., warm, temperate – climate, with hot summers, dry and cold winters, and four distinct seasons. The annual average temperature of the area is 14.4 °C, with relative humidity near 70%. The area of dominant wind direction is easterly. The wind speed is the highest in spring, with winter and the lowest in autumn. In April of the year, the average wind speed is the highest, with a regional average

of 3.7 m/s. Annual average precipitation and evaporation are 858.1 and 1589.4 mm, respectively, and the precipitation is mainly concentrated in June to August (Figure 1c).

The Pearl Lake (Figure 1d), named after Pearl Buck, is in the east campus of Suzhou University at E117°4′ and N33°38′. It is artificial, and almost 160 m north to south, and between 26 and 65 m west to east. The total surface area is near 7000 m². The depth of water is 1 to 4 m at different times but mostly about 2 to 2.5 m. Precipitation and pumped recharge (to maintain the water level) are main sources of water, and water loss occurs mainly by evaporation. In addition, there is a small river which is 20 meters away from Pearl Lake. It is located in the middle of the East Campus of Suzhou University, with a depth of 1–1.5 m, a width of about 6 m and a flow rate of 0.01 m/s. The stream belongs to a branch of another river.

1.2. Sampling and analyses

20 samples were collected from Pearl Lake on May 5 and June 5, 2019 (10 samples each time – for locations and site numbers see Figure 1d). The daily minimum and maximum temperatures were 10–25 and 20–38 °C. There was no rainfall during the period but the weather was sunny or cloudy (the historical weather data are available at https://lishi.tianqi.com/suzhou1/201906.html). No pumping occurred during the period, either.

The samples were collected in polyethylene bottles cleaned in the laboratory, and the locations and other information were recorded during sampling. After collection, all samples were filtered through 0.45 μ m microporous membrane, and the stable hydrogen and oxygen isotopes were measured by liquid isotope analyzer (LGR iwa-45ep), the accuracies are $\delta D < 0.5 \%$, and $\delta^{18}O < 0.1 \%$, respectively. The results were then calculated with VS-MOW standard. The analytical quality is controlled by



Figure 1. Study area location (Pearl Lake)

the standard sample, and the relative standard deviation is within 5%. All measurements were processed in the Key Laboratory of Mine Water Resource Utilization of Anhui Higher Education Institute.

1.3. Description of isotopic model

Previous studies have suggested that the quantitative influence of evaporation can be calculated from the quantitative change of residual relative to initial water, via the hydrogen and oxygen isotope composition (δ) (Dansgaard, 1964; Kim & Lee, 2011; Zhang & Zheng, 2011). Under Rayleigh equilibrium evaporation conditions, there is an exponential relationship between f (volume of residual water relative to initial water body) and hydrogen and oxygen isotope composition (δ). It obeys the Rayleigh evaporation and fractionation model (Dansgaard, 1964; Kim & Lee, 2011; Zhang & Zheng, 2011) – Eq. (1):

$$\delta = (\delta_0 + 1)f^{(a-1)} - 1, \tag{1}$$

where the initial value is δ_0 , and the fractionation coefficient is a. The value where the evaporation line intersects the local meteoric water line is often taken as δ_0 . δ is the measured values. If the absolute value of δ in Eq. (1) is small, that equation can be simplified to Eq. (2):

$$\delta - \delta_0 = 10^3 (a - 1) \ln f. \tag{2}$$

Under Rayleigh equilibrium evaporation conditions, temperature is the main factor controlling hydrogen and oxygen isotope fractionation, and the relationships between temperature, T (°K) and the fractionation coefficient are determined using Eqs (3) and (4):

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

$$10^{3} \ln a D = 24.844 (10^{6}/T^{2}) - 76.248 (10^{3}/T) + 52.612. (4)$$

2. Results and discussion

2.1. Compositions of hydrogen and oxygen isotopes

The stable hydrogen and oxygen isotopic compositions of Pearl Lake water samples are shown in Table 1. The δ^{18} O and δ D of the May samples were between -2.13 and -3.65‰, and -25.89 and -31.16‰, respectively. In June, the δ^{18} O of the samples was between -1.32 and -2.43‰, and δ D between -21.01 and -24.58‰.

Table 1. Hydrogen and oxygen stable isotopic compositions

Sample ID	May 5			June 5		
	δ ¹⁸ O/‰	δD/‰	d-excess	δ ¹⁸ O/‰	δD/‰	d-excess
ZZ-01	-2.93	-30.57	-7.10	-1.53	-23.86	-11.58
ZZ-02	-3.07	-30.51	-5.92	-1.74	-23.89	-9.97
ZZ-03	-2.93	-30.76	-7.32	-1.57	-23.67	-11.12
ZZ-04	-2.48	-31.16	-11.30	-1.42	-23.86	-12.51
ZZ-05	-2.13	-29.47	-12.47	-1.75	-23.23	-9.20
ZZ-06	-2.77	-29.58	-7.43	-1.32	-24.58	-13.99
ZZ-07	-2.29	-30.89	-12.56	-1.54	-23.86	-11.53
ZZ-08	-2.52	-30.08	-9.89	-2.61	-21.01	-0.15
ZZ-09	-2.62	-30.31	-9.37	-2.41	-21.99	-2.70
ZZ-10	-3.65	-25.59	3.63	-2.43	-21.66	-2.19

Note: d-excess = $\delta D - 8 \times \delta^{18} O$.

Figure 2 shows the differences in hydrogen and oxygen stable isotope concentrations in different months and locations (at the same time). The $\delta^{18}O$ and δD of all samples except ZZ-08 increased between May and June, which indicates evaporation as the cause. The $\delta^{18}O$ of ZZ-08 fell slightly while δD increased from May to June, perhaps because of the relatively low extent of evaporation. Sample ZZ-09 has a similar signature (a small increase in $\delta^{18}O$ but a significant one in δD). As can be seen from the Figure 1d-III, ZZ-08 and -09 were collected in the south part of the lake, both locations were shaded because of the direction (from south to north) of sunlight at the time. A similar conclusion can also be drawn about ZZ-05 (slight increase in $\delta^{18}O$ but significant one in δD), which was collected north of the bridge, in an area shaded by the bridge (Figure 1d-I).

2.2. Relationships between $\delta^{18}O$ and δD

The global meteoric water line (GMWL: $\delta D = 8\delta^{18}O + 10$) was first proposed by Craig (1961), since when a series of studies related to the local meteoric water lines have been carried out, showing that the lines were different in different regions or under different climatic conditions. Therefore, when the hydrogen and oxygen isotopes are studied, the local meteoric water line should be taken as the reference. However, Suzhou's local meteoric water line is not yet reported, so the national meteoric water line of



Figure 2. Changes in lake water δ^{18} O and δ D compositions

China (NMWL) (Zhang & Wang, 2016; Singh, 2014) has been applied in this study. The meteoric water line equation is presented as Eq. (5):

$$\delta D = 7.9 \delta^{18} O + 8.2. \tag{5}$$

Moreover, in order to highlight the influence of evaporation in a more detailed way, the evaporation line for the mining area (MEL) in northern Anhui Province reported by Chen et al. (2008) was adopted in this study, as shown in Eq. (6):

$$\delta D = 5.89 \delta^{18} O - 7.68. \tag{6}$$

As can be seen from the Figure 3, all Pearl Lake water samples plot to the right of NMWL, indicating that the lake's water is affected by evaporation.



Figure 3. Relationship between lake water δ^{18} O and δ D

2.3. d-excess

In order to compare the differences between global and regional meteoric water, Dansgaard (1964) proposed the concept of deuterium excess (d-excess), defined by Eq. (7):

d-excess = $\delta D - 8 \times \delta^{18} O.$ (7)

The parameter has been widely used in groundwater studies because the hydrogen component concentrations in rocks are very low and generally do not cause changes in the water, but water-rock interactions can influence the δ^{18} O of the water with temperature >60 °C, when the groundwater's d-excess will decrease. Previous studies have shown that the d-excess is related with source moistures or evaporation processes (Jouzel et al., 2013). The variations of d-excess can be applied to the study of surface water, whose hydrogen and oxygen isotopes can be affected by evaporation, leading to variations of d-excess. The δD and $\delta^{18}O$ increase during evaporation, and the d-excess is controlled by variation rates. If the increasing rate of δD is higher than the $8 \times \delta^{18} O$, the d-excess will increase, while if the increasing rate of δD is lower than the $8 \times \delta^{18}$ O, the d-excess will decrease. For the Pearl Lake water samples, the May and June d-excess values range



Figure 4. Changes in d-excess

from -12.56 to 3.63% and -13.99 to -0.15%, respectively (Table 1), which are lower than the d-excess value of the GMWL (Figure 4), indicating that the water isotopes might have been affected by evaporation.

The change range of d-excess values, by Table 1 calculations, is -6.56 to 9.74‰: six have decreased and four increased. Two hydrogen isotopes (¹H and ²H) are related to δD , and two oxygen ones (¹⁶O and ¹⁸O) related to $\delta^{18}O$. With low evaporation (e.g. low temperatures or in shaded areas), the hydrogen isotopes are more easily influenced than those of oxygen, because the hydrogen isotope masses are lower than those of the oxygen isotopes. As evaporation increases, the differential fractionation between hydrogen and oxygen isotopes decreases. Thus, if the change in δD exceeds that of $8 \times \delta^{18}O$ – i.e., the evaporation intensity is low – the increase in δD will exceed $8 \times \delta^{18}O$, leading to an increase in d-excess, while strong evaporation can lead to a fall in d-excess.

While δD and $\delta^{18}O$ increased in all water samples except for ZZ-08, their changing rates differ, causing both increasing (ZZ-05, 07, 08 and 09) and decreasing (ZZ-01, 02, 03, 04, 06 and 10) d-excess. Consideration of the sampling locations shows that those for which d-excess values increased are shaded by trees and a bridge, while the others came from areas with direct sunlight.

2.4. Quantity of residual water relative to initial water

In this study, the E/I ratio (evaporation-to-input ratio) that was calculated by the relative humidity was 0.40. The δ_0 was calculated from the intersection of Eqs (5) and (6). The results are $\delta_0^{18}O = -7.91\%$, $\delta_0D = 54.25\%$, δ is the measured values listed in Table 1. The temperature at the time of sampling was 27 °C, from which the fractionation coefficient was calculated as 1.0092. Previous studies showed that it is better to use $\delta^{18}O$ than δD to calculate the quantity of evaporation (Wu & Wang, 2011), which was then done in this study – see Figure 5. As can be seen, the residual water quantity was 53 to 63% during the May sampling, indicating that 37 to 47% of the water had evaporated relative to the initial volume. In June, the



Figure 5. Relationships between the proportion of residual water and $\delta^{18}O$

residual water quantity was 49 to 56% – i.e., 44 to 51% of the water had evaporated.

In other words, between May 5 and June 5, some 1 to 8% (mean 5%) of the water evaporated. A comparative study of a small river nearby showed that between 1 and 24% (mean 10%) of its water had evaporated over the same period (data not shown), suggesting that the influence of evaporation on the different water bodies is different.

Conclusions

On the basis of the hydrogen and oxygen isotopes in water samples collected in Pearl Lake during May and June:

(1) Most of the samples had higher δ^{18} O and δ D values in June than May, implying that the water's hydrogen and oxygen isotope ratios 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 variations of d-excess are controlled by the water environment – e.g., whether it is shaded or not.

(3) Calculations based on Rayleigh equilibrium evaporation showed that residual water quantities were 53 to 63% and 49 to 56% for May and June relative to the initial quantities, indicating that about 5% of the water evaporated during the period between May 5 and June 5.

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