ESTIMATION OF EVAPORATION RATE OF SURFACE WATER USING HYDROGEN AND OXYGEN ISOTOPIC RATIOS

Masahiro Yamashita[1] and Hiroyuki Ii[2]

[1]Graduate School of Systems Engineering, Wakayama University, Japan; [2]Faculty of Systems Engineering, Wakayama University, Japan

ABSTRACT: Both evaporation rate and temperature can be estimated from δD and $\delta^{18}O$ values of water before and after evaporation. From laboratory evaporation test results of water under uniform temperature condition, relations between evaporation rate, δD and $\delta^{18}O$ values of water before and after evaporation were expressed at each temperature as the following equations, $Y = -0.44X1 + 12.67X2 + 50.90 : 20$ degrees C, $Y = 0.30X1 + 1.88X2 + 41.86 : 25$ degrees C, $Y = -1.70X1 + 11.80X2 + 7.74 : 30$ degrees C, $Y = -0.11X1 + 6.37X2 + 34.74 : 35$ degrees C, $Y = -0.71X1 + 6.82X2 + 35.11 : 40$ degrees C and $Y = -0.17X1 + 4.94X2 + 30.05 : 50$ degrees C. Y is evaporation rate. X1 is $\delta Dae - \delta Dbe - 51.3$. X2 is $\delta^{18}Oae - \delta^{18}Obe -7.52$. δDbe and δDae are δD values of water before and after evaporation. $\delta^{18}Obe$ and $\delta^{18}Oae$ are $\delta^{18}O$ values of water before and after evaporation. Evaporation temperature can be also estimated from δD and $\delta^{18}O$ values of water before and after evaporation. Relation was expressed by the equation, $(\delta Dae - \delta Dbe - 51.3) / (\delta^{18}Oae - \delta^{18}Obe -7.52) = -0.064 \times$ temperature $+ 7.45$. From δD and $\delta^{18}O$ distribution map of water before and after evaporation, both evaporation rate and temperature can be also estimated.

Keywords: Evaporation rate, Hydrogen isotopic ratio, Oxygen isotopic ratio, Evaporation experiment

1. INTRODUCTION

One of the biggest environmental problems in the 21st century is the depletion of water resources. As a result of global warming, it is considered that the amount of usable water will decrease due to evaporation of surface water. Resultantly, it is very important to grasp evaporation rates in order to improve management of water resources for dams, reservoirs and irrigation water, etc. There are various methods to calculate evaporation rates such as the Thornthwaite method [1] and the Penman method [2], etc. The relation between evaporation and isotope is discussed [3], [4]. The estimation method of evaporation rate using isotopic ratio was made by Allison et al. [5] or Gibson et al. [6]. However using their methodology is not easy because they need complex parameters as shown in this example equation (1) [7], [8].

$$\frac{d\,\delta_L}{d\ln f} = \frac{h_A(\delta_L - \delta_A)/(1 + \delta_L) - \varepsilon^*}{(a - h_A)(a \cdot \alpha_{vap-liq} \cdot e_{i,L}/e + e_i/e)} \quad (1)$$

δ_L : isotopic ratio of water
f : volume ratio of remain water per original water
δ_A : isotopic ratio of vapor
h_A : humidity
a : water activity
ε^* : $a\varepsilon + \triangle\varepsilon$ (ε : equilibrium, vapor pressure ratio,
$\triangle\varepsilon$: amount of change equilibrium vapor pressure ratio)
$\alpha_{vap-liq}$: partition coefficient
$e_{i,L}$: diffusion resistance of heavy water in water

e : diffusion steam resistance in atmosphere (Constant), e_i : diffusion resistance of heavy water in atmosphere

In the past, using an oxygen isotopic ratio, a simple estimation of evaporation was carried out [9] however, neither the hydrogen isotopic ratio (δD) nor the oxygen isotopic ratio ($\delta^{18}O$) were clarified. Generally, δD and $\delta^{18}O$ values in rain water are located in the vicinity of the meteoric water line ($\delta D=8\times\delta^{18}O+10$) (Fig.1). When water evaporates, both δD and $\delta^{18}O$ values increase, however the isotopic ratio, δD per $\delta^{18}O$, decreased from 8 to lower values. The ratio depends on the evaporation temperature and differences of δD and $\delta^{18}O$ values between before evaporation and after evaporation, and increases with evaporation rate as shown in Fig.1 [8]. Therefore, it was thought that evaporation rate could be calculated from the difference values. The purpose of this study was to clarify the relationship between evaporation rate, isotopic ratios, humidity and temperature by using these properties and to propose a simple estimation method.
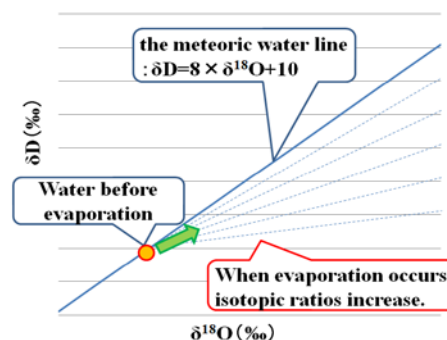

Fig. 1   Change of δD and $\delta^{18}O$ due to evaporation

2. METHOD

The experiment was performed in a thermostatic chamber (SANYO MIRI153: Fig.2). In this experiment, the temperature of the thermostatic chamber was changed from 20 to 50 degrees C. Temperature and humidity during the experimental period were recorded every 30 minutes by the storage meter (SATO METER WORKS SK-L200TH2: Fig.3). The tap water, equaling 2000 g which was put in a polyethylene bottle of capacity 2 L evaporated. The polyethylene bottle was 126 mm diameter, 245 mm height and 75 mm diameter at the mouth. The weight of the residual tap water was measured and tap water was sampled once every few days until it dried up. The experimental process is as shown in Fig.4.

Fig. 2 Thermostatic chamber

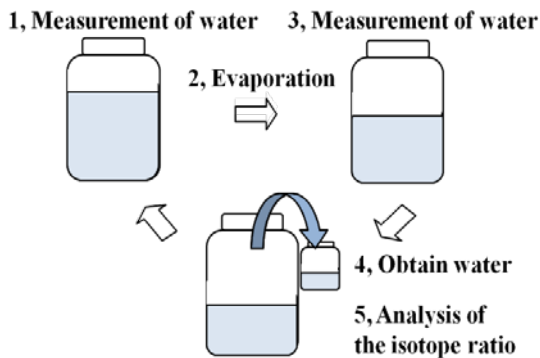Fig. 3 Storage meter of temperature and humidity

Fig. 4   Process of evaporation experiment

The measurement of δD and $\delta^{18}O$ was carried out in an isotopic ratio measurement system (Sercon Geo Wet System: Fig.5). δD and $\delta^{18}O$ are presented as per mil (‰) of the standard average seawater (SMOW: Standard Mean Ocean Water). The formulas are shown in equation (2) and (3). δD and $\delta^{18}O$ of SMOW are denoted as $(D/H)_{SMOW}$, $(^{18}O/^{16}O)_{SMOW}$ and δD and $\delta^{18}O$ of the sample are denoted as $(D/H)_{Sample}$, $(^{18}O/^{16}O)_{Sample}$. Measurement error of δD is ±1.0 ‰ and measurement error of $\delta^{18}O$ is ±0.1 ‰.

$$\delta D = [(D/H)_{Sample}/(D/H)_{SMOW}-1] \times 1000: \quad (2)$$

$$\delta^{18}O = [(^{18}O/^{16}O)_{Sample}/(^{18}O/^{16}O)_{SMOW}-1] \times 1000: \quad (3)$$

Fig.5 Isotopic ratio measurement system (Sercon Geo Wet System)

3. RESULT

The temperature in the thermostatic chamber was varied in 5 degrees C intervals from 20 degrees C to 50 degrees C excluding 45 degrees C. Tap water equaling 2000 g was evaporated and taken until it dried up at each temperature condition. The water sampling period for each temperature are as follows.

- 20 degrees C: 16/04/2014~01/07/2014
- 25 degrees C: 17/12/2014~03/03/2015
- 30 degrees C: 04/03/2014~15/04/2014
- 35 degrees C: 28/07/2014~29/08/2014
- 40 degrees C: 16/01/2014~04/02/2014
- 50 degrees C: 20/10/2014~09/12/2014

Table1 shows the number of collected samples, average measured temperature and average humidity at each temperature. The total number of evaporation experiments was 113.

Fig. 6 shows the relationship between evaporation rate and δD at 20, 25, 30, 35, 40 and 50 degrees C. δD value of the tap water before evaporation was -52.3 to -50.3 ‰. In five experiments excluding 20 degrees C, δD values increased and in particular after 60 to 80 % evaporation rate, they increased remarkably. However, at 20 degrees C, although δD values

increased in the same way until 60 % evaporation rate, they decreased with evaporation after 70 % evaporation rate. δD values at 30 degrees C in Fig.8 rose to 172.1 ‰ finally. This was the largest increase among all the 113 samples.

Table1 Summary of each temperature

preset temperature	20℃	25℃	30℃	35℃	40℃	50℃
number of sumples	40	18	19	7	22	7
average temperature (℃)	19.7	23.8	29.8	34.9	39.3	49.1
average humidity (%)	64.2	32.6	29.6	43.9	29.0	30.3
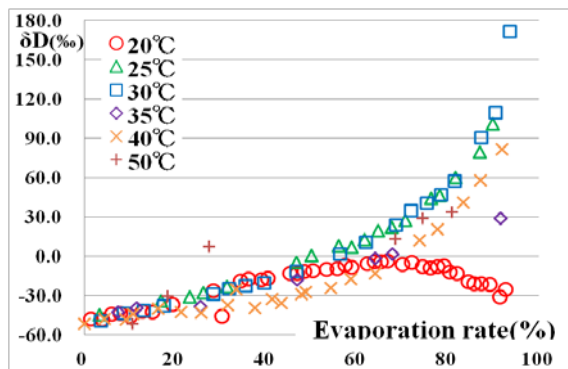
Fig.6   Relationship between evaporation rate and δD at each temperature
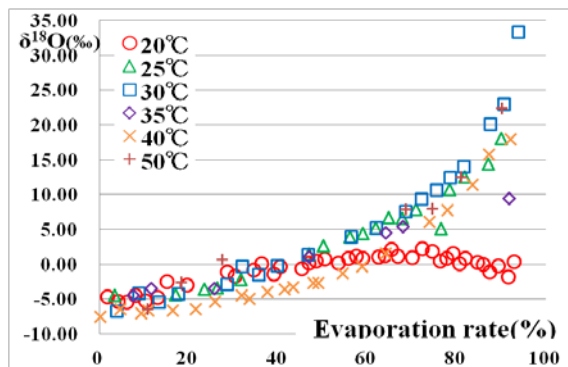
Fig.7   Relationship between evaporation rate and δ18O at each temperature

Fig.7 shows relationship between evaporation rate and $\delta^{18}O$ at 20, 25, 30, 35, 40 and 50 degrees C. $\delta^{18}O$ value of the tap water before evaporation was -7.66 to -7.39 ‰. $\delta^{18}O$ at 30 degrees C in Fig.14 rose to 33.44 ‰ finally, it was the largest increase among all the 113 samples. $\delta^{18}O$ values at 25, 30, 35, 40 and 50 degrees C increased with evaporation rate and in particular after 50 % evaporation rate remarkably

increased as well as δD values. At 20 degrees C, $\delta^{18}O$ values decreased after 70 % evaporation rate. Typically, the hydrogen and oxygen isotopic ratio increased when evaporation proceeded. However, a decrease with evaporation rate of both δD and $\delta^{18}O$ values was observed at 20 degrees C. Comparing 20 degrees C and other temperature conditions, the average humidity of the experiment of 20 degrees C was 64.2 %, higher than those under other temperature conditions. Therefore, humidity maybe a critical parameter which controls δD and $\delta^{18}O$ values. Therefore, it is necessary to consider its influence under high humidity conditions.
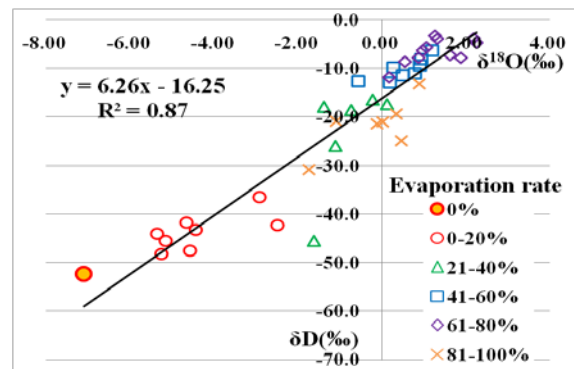

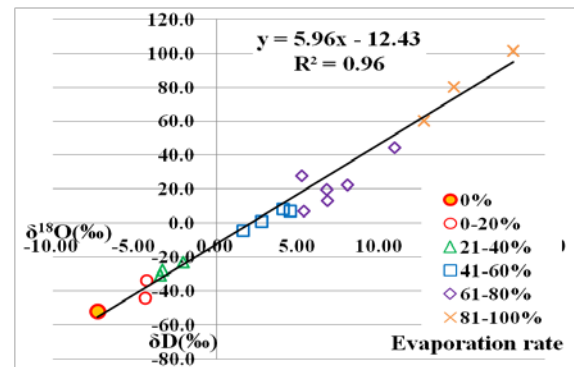Fig.8   Relationship between δD and $\delta^{18}O$ at 20 degrees C

Fig. 9   Relationship between δD and $\delta^{18}O$ at 25 degrees C

4. DISCUSSION

Fig.8, 9, 10, 11, 12 and 13 show the relationship between δD and $\delta^{18}O$ at each temperature. Most of δD/$\delta^{18}O$ values were distributed on one approximate straight line. However, each slope of the approximate line for δD/$\delta^{18}O$ values at each temperature was different. The slope value depended on temperature and it varied from 4.40 at 50 degrees C to 6.26 at 20 degrees C. Fig.14 shows the relationship between temperature of evaporation and the slope of line for δD/$\delta^{18}O$ at the experiments.
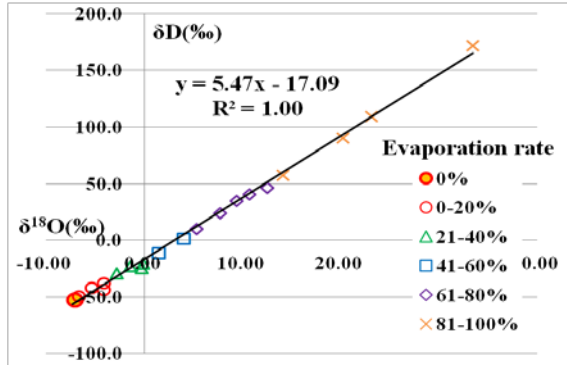
Fig.10   Relationship between δD and δ^{18}O at 30 degrees C
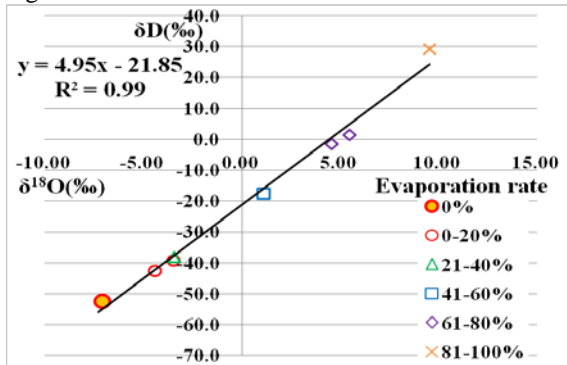

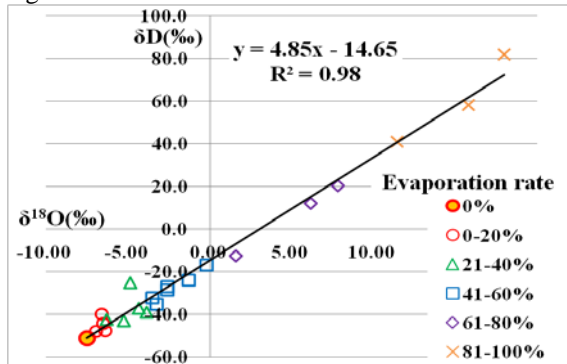Fig.11   Relationship between δD and δ^{18}O at 35 degrees C

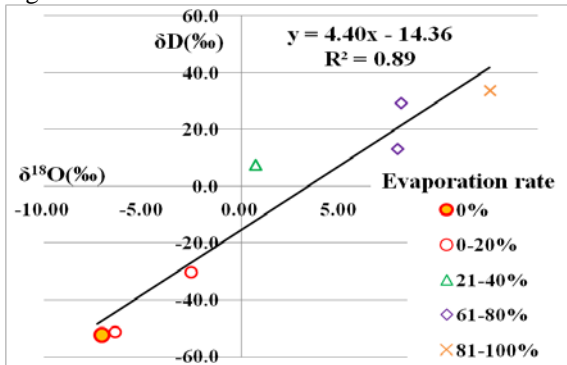Fig.12   Relationship between δD and δ^{18}O at 40 degrees C

Fig.13   Relationship between δD and δ^{18}O at 50 degrees C

As the slope of the meteoric water line (δD=8×δ^{18}O+10) is 8.00, it was found that δD/δ^{18}O values decreased from 8.00 for the meteoric line with the temperature rising. δD/ δ^{18}O values were 6.26 at 20 degrees C, 5.96 at 25 degrees C, 5.47 at 30 degrees C, 4.95 at 35 degrees C, 4.85 at 40 degrees C and 4.40 at 50 degrees C. As a result of regression analysis, the slope, δD/ δ^{18}O value was determined as the following equation when the original δD and δ^{18}O before evaporation was -52.3 to -50.3 ‰ and -7.66 to -7.39 ‰.

$$\delta D / \delta^{18}O = -0.064 \times temperature + 7.45 \qquad (4)$$

Therefore, evaporation temperature can be estimated from multiple δD/ δ^{18}O values of water although multiple δD/ δ^{18}O values at different evaporation rates are necessary for analysis. If a change in isotope values per evaporation rate stays uniform under different original isotope values of water before evaporation, a general equation can be calculated based on equation.

$$(\delta Dae - \delta Dbe - 51.3) / (\delta^{18}Oae - \delta^{18}Obe -7.52)$$
$$= -0.064 \times temperature + 7.45 \qquad (5)$$

δDbe is the δD value of water before evaporation and δDae is the δD value of water after evaporation. Similarly δ^{18}Obe is the δ^{18}O value of water before evaporation and δ^{18}Oae is the δ^{18}O value of water after evaporation.

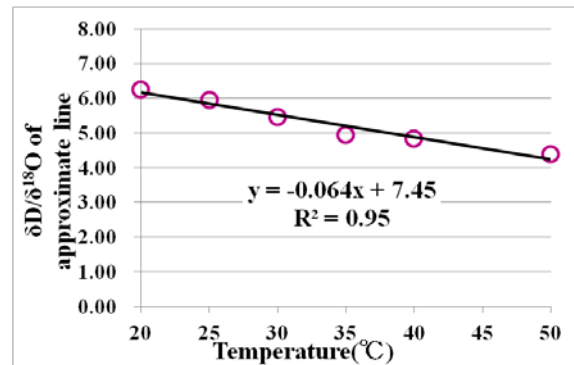
Fig.14   Relationship between temperature of evaporation and δD/δ^{18}O of approximate line

Next, the influence of humidity on evaporation rate, δD/ δ^{18}O and temperature was clarified. Fig.15 and Fig.16 show the changes of δD and δ^{18}O values per evaporation rate at 0 to 30 %, 31 to 50 % and 51 to 100 % humidity. Excluding some data, the change of δD per unit evaporation rate was -1 to 1 % / ‰, uniform with evaporation rate. The change of δD value per unit evaporation rate was uniform under variable humidity condition. Similarly, the change of δ^{18}O values per unit evaporation rate was uniform at 0 to 30 % humidity although δ^{18}O values per unit

evaporation rate under the higher humidity condition were variable. However, a clear relation between humidity and $\delta^{18}O$ values per unit evaporation rate was not observed. Therefore, it is not necessary to consider the effect of humidity when evaporation rate is determined using δD and $\delta^{18}O$ values.
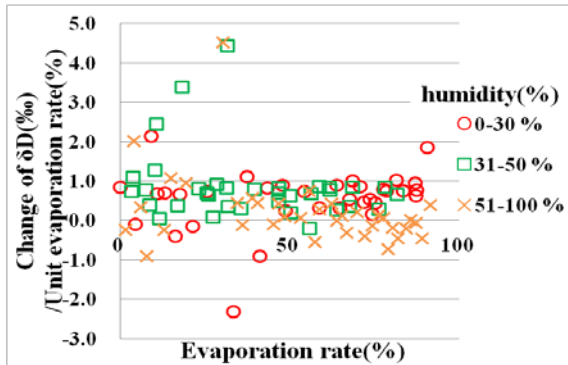

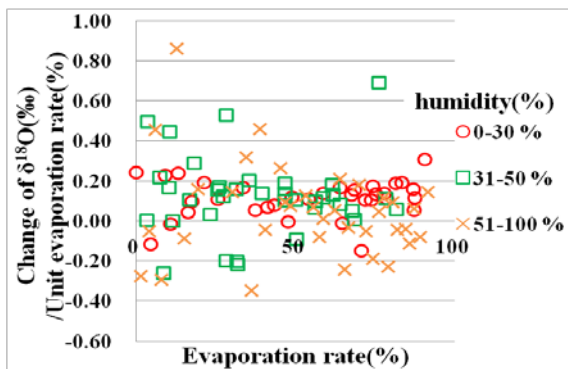Fig.15 The changes of δD values per unit evaporation rate at each level of humidity

Fig.16 The changes of δD values per unit evaporation rate at each level of humidity

In this experiment, it was found that δD and $\delta^{18}O$ were affected by temperature and were not affected by humidity. Based on the results of Fig.8, 9, 10, 11, 12 and 13, a regression analysis was performed using temperature, δD and $\delta^{18}O$ values before and after evaporation excluding humidity. The calculated relations were expressed at each temperature as the following equation (6), (7), (8), (9), (10), and (11).

$$Y = -0.44X1 + 12.67X2 + 50.90 \; : 20 \text{ degrees C} \quad (6)$$

$$Y = 0.30X1 + 1.88X2 + 41.86 \; : 25 \text{ degrees C} \quad (7)$$

$$Y = -1.70X1 + 11.80X2 + 7.74 \; : 30 \text{ degrees C} \quad (8)$$

$$Y = -0.11X1 + 6.37X2 + 34.74 \; : 35 \text{ degrees C} \quad (9)$$

$$Y = -0.71X1 + 6.82X2 + 35.11 : 40 \text{ degrees C} \quad (10)$$

$$Y = -0.17X1 + 4.94X2 + 30.05 : 50 \text{ degrees C} \quad (11)$$

Y is evaporation rate. X1 is δD and X2 is $\delta^{18}O$ of water after evaporation when the original δD and $\delta^{18}O$ before evaporation was -52.3 to -50.3 ‰ and -7.66 to -7.39 ‰.

Fig.17 shows actual evaporation rate and calculated evaporation rate using D and $\delta^{18}O$ from equation (6) to (11) when the original δD and $\delta^{18}O$ before evaporation was -52.3 to -50.3 ‰ and -7.66 to -7.39 ‰. A good agreement between the actual evaporation rate and the calculated evaporation rate was observed under variable temperature conditions although the difference was less than $\pm$ 10 %. Therefore, it is concluded that it is possible to measure the evaporation rate by using δD, $\delta^{18}O$ and temperature during evaporation.

As the equation (6) to (11) was determined when the original δD and $\delta^{18}O$ before evaporation was -52.3 to -50.3 ‰ and -7.66 to -7.39 ‰. If the change of isotope values per evaporation rate remains uniform under different original isotope values of water before evaporation, a general equation can be calculated based upon equation (6) and (13).

$$X1 = \delta Dae - \delta Dbe - 51.3 \quad (12)$$

$$X2 = \delta^{18}Oae - \delta^{18}Obe - 7.52 \quad (13)$$

δDbe is the δD value of water before evaporation and δDae is the δD value of water after evaporation. Similarly $\delta^{18}Obe$ is the $\delta^{18}O$ value of water before evaporation and $\delta^{18}Oae$ is the $\delta^{18}O$ value of water after evaporation.

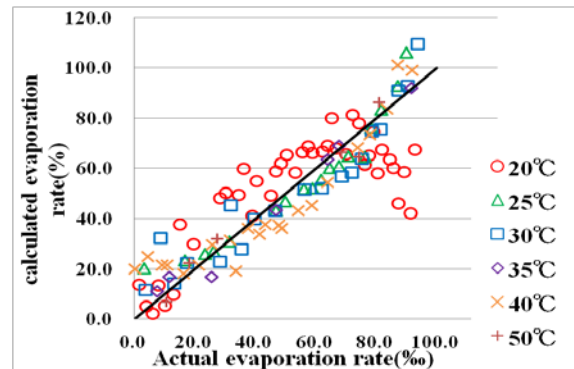
Fig.17 Actual evaporation rate and calculated evaporation rate using D and $\delta^{18}O$

From Fig.14, the slope, $\delta D/ \delta^{18}O$ value during evaporation was determined as the following equation, y = -0.064x + 7.45 (x: temperature, y: $\delta D/ \delta^{18}O$) and then the difference of δD and $\delta^{18}O$ values between before and after evaporation indicated evaporation rate shown as equation (6) to (13). Therefore, temperature and evaporation distribution map with δD and $\delta^{18}O$ values of water was made as shown in Fig18. Fig.18 shows δD and $\delta^{18}O$ values of water after evaporation with evaporation rate and

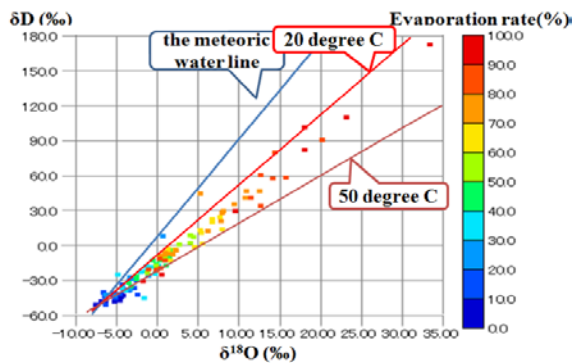temperature. From Fig.18, both evaporation temperature and evaporation rate can be estimated easily.

Fig.18 Relationship between δD, δ¹⁸O and evaporation rate

5. CONCLUSION

By conducting an evaporation test of water in the laboratory under uniform temperature conditions, the relation between δD and δ¹⁸O values of water before and after evaporation, evaporation rate, temperature and humidity was clarified.

It was found that δD and δ¹⁸O values of water after evaporation changed with evaporation rate, and were affected by temperature and not humidity. Resultantly, under each temperature, evaporation rate can be estimated from δD and δ¹⁸O values of water before and after evaporation. The calculated relations between evaporation rate, δD and δ¹⁸O values of water before and after evaporation were expressed at each temperature as the following equations, $Y = -0.44X1 + 12.67X2 + 50.90$: 20 degrees C, $Y = 0.30X1 + 1.88X2 + 41.86$: 25 degrees C, $Y = -1.70X1 + 11.80X2 + 7.74$: 30 degrees C, $Y = -0.11X1 + 6.37X2 + 34.74$: 35 degrees C, $Y = -0.71X1 + 6.82X2 + 35.11$: 40 degrees C and $Y = -0.17X1 + 4.94X2 + 30.05$: 50 degrees C. Y is evaporation rate. X1 is δDae – δDbe – 51.3. X2 is δ¹⁸Oae - δ¹⁸Obe - 7.52. δDbe is δD value of water before evaporation. δDae is δD value of water after evaporation. δ¹⁸Obe is δ¹⁸O of water before evaporation. δ¹⁸Oae is δ¹⁸Ovalue of water after evaporation.

Evaporation temperature can be also estimated from δD and δ¹⁸O values of water before and after evaporation. This relation was expressed by the equation, $(δDae – δDbe – 51.3) / (δ^{18}Oae - δ^{18}Obe - 7.52) = -0.064 \times temperature + 7.45$.

Therefore, both evaporation rate and temperature can be estimated from δD and δ¹⁸O values of water before and after evaporation. From δD and δ¹⁸O distribution map of water before and after evaporation, both evaporation rate and temperature can be also estimated.

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Corresponding Author: Masahiro Yamashita