water

MDPI

Article

Influencing Factors and Calibration of the Direct Vapor Equilibration Method for Measuring Soil Water Isotopes

Zhenguo Xing [1,2,3,4,5,*], Ruimin He [1,2,5], Jie Fang [3,4,5], Lu Bai [3,4,5], Xuejia Li [1,2], Xiaoqing Liu [1,2], Gang Liu [1,2] and Mingjing Zhou [6,*]

1 State Key Laboratory of Water Resource Protection and Utilization in Coal Mining, Yulin 719315, China
2 China Energy Shendong Coal Group Co., Ltd., Technology Research Institute, Yulin 719315, China
3 National Institute of Clean-and-Low-Carbon Energy, Beijing 102211, China
4 State Key Laboratory of Water Resource Protection and Utilization in Coal Mining, National Institute of Clean-and-Low-Carbon Energy, Beijing 102209, China
5 China Energy Investment Group, Beijing 100011, China
6 Key Laboratory of Agricultural Soil and Water Engineering in Arid and Semiarid Areas, Ministry of Education, Northwest A&F University, Yangling 712100, China
* Correspondence: 20039424@ceic.com (Z.X.); zhoumingjing0903@163.com (M.Z.)

Abstract: The direct vapor equilibration-laser spectroscopy (DVE-LS) method can be used to measure the stable isotopes of soil water (δ^2H and $\delta^{18}O$), a technique that is easier to operate and quicker for sampling compared to the traditional cryogenic vacuum distillation (CVD) method. However, the soil water isotope values thus obtained often deviate from the true value, which is affected by the equilibrium temperature during the measurement process. Therefore, this study conducted an indoor experiment on five soil samples of varying textures. The dry soil was wetted by reference water samples to four different soil water content (SWC) values and then equilibrated at five different temperatures. The soil water isotope deviation value (SWIDV) of the DVE-LS method was determined by building a correction equation between SWIDV and the influencing factors (equilibrium temperature, soil clay content (SCC), and SWC, after which the correction equation values were compared to those calculated by the CVD method for the field-collected soil samples to check the accuracy. The results shows that the $\Delta\delta^2H$ value increased with increasing equilibrium temperature and soil clay content, but decreased with increasing SWC. The multi-factor variance analysis shows that equilibrium temperature, SCC, and SWC significantly affected the $\Delta\delta^2H$ values and deviation values with the DVE-LS method, but insignificantly affected the $\Delta\delta^{18}O$ values and deviation values. The correction equations (3) was built at different equilibrium temperatures, and the RMSE decreased from 4.07‰ to 1.24‰ and from 8.99‰ to 4.14‰, respectively, as calibrated by the isotope values of soil samples collected in Changwu and Suide counties. The correction equations under various equilibrium temperatures increased the accuracy of the DVE-LS method in obtaining soil water isotope values and promoted the application of the DVE-LS method in soil water isotope analysis.

Keywords: water vapor balance method; soil water isotope; equilibrium temperature; soil characteristics; correction method

check for updates

Academic Editor: Daniel D. Snow

Received: 27 November 2024
Revised: 23 December 2024
Accepted: 29 December 2024
Published: 4 January 2025

Citation: Xing, Z.; He, R.; Fang, J.; Bai, L.; Li, X.; Liu, X.; Liu, G.; Zhou, M. Influencing Factors and Calibration of the Direct Vapor Equilibration Method for Measuring Soil Water Isotopes. *Water* **2025**, *17*, 116. https://doi.org/10.3390/w17010116

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Soil is a key element in the continuous atmosphere-plant-groundwater moisture cycle. Therefore, understanding the movement processes of soil moisture can provide guidance for hydroecological studies and agricultural production [1,2]. The stable isotopes ^2H and ^{18}O

found in water can be used as a natural tracer. The stable isotope tracer method has become more fully established since the study of stable isotopes in atmospheric precipitation began in 1953. It is now commonly used in ecohydrology to investigate how water moves [3]. In the application of water stability isotope research, the sampling and water extraction processes often become limiting factors to the accuracy of isotope analysis [4]. The accuracy of the results is directly affected by the extraction rate of the different methods and whether distillation occurs during the extraction process, which, in turn, affects the determination and analysis of oxygen isotopes [5].

There are currently two main methods for obtaining soil water isotope information. One is to use the water vapor equilibrium method to connect the isotope laser spectrometer (direct vapor equilibration laser spectrometer, DVE-LS) to directly determine the isotopic composition of soil water vapor and calibrate it to liquid water isotope values using standard samples. The other method is to first extract water from the soil, including by cryogenic vacuum distillation (cryogenic vacuum distillation, CVD) [6], the suction gauge method [7,8], azeotropic distillation method [9], high-speed centrifugation method [10,11], and mechanical pressing method [12], and then to use isotope mass spectrometry or isotope laser spectrometry to determine the isotopic composition of the soil water. Among the many methods for extracting soil water, the CVD method has been widely recognized by many scholars as a method that can extract all the pore water in the soil; it is also the most widely used method [13–15]. The operation of DVE-LS is easier and the sampling efficiency is higher, and the technique can be used for high-spatial and temporal resolution during in situ water isotope monitoring [16–18], which can also be useful for a wider range of purposes [16].

A device called an isotope mass spectrometer is necessary to determine the values of δ^2H and $\delta^{18}O$ in water. This is achieved by measuring the gas when it is in equilibrium with CO_2 or H_2 [19,20]. With the development of laser spectroscopy, easily accessible dry gases can be used as a reference, and δ^2H and $\delta^{18}O$ can be obtained simultaneously [21]. The first time that isotope laser spectroscopy was combined with the vapor pressure equilibrium method was achieved by Revesz et al. (1990), who promoted the application of direct vapor pressure equilibrium and laser spectroscopy as combined methods [9]. However, the DVE-LS method for finding out about soil water stable isotopes is affected by factors like container material [5,12,22], water vapor concentration [21,23], soil texture, equilibrium temperature, and more, which can cause mistakes in the measurements. These measurement errors are mainly reduced by improving the experimental methods and perfecting correction methods. Wassenaar et al. (2008a) used glass bottles with good airtightness to reduce the bias caused by leaking Ziploc® bags [21], polyester film bags, etc. Wassenaar et al. (2008a) and Hendry et al. (2015) found that ensuring that the soil sample moisture content was no less than 0.05 g g^{-1} could reduce the bias caused by low water vapor concentrations in the measurement of isotopes [12,21]. If you use the vapor pressure equilibrium method to determine the isotopic composition of soil water, you need to make sure that both the soil sample and the standard sample have the same amount of water vapor in them. This will remove the effect of the water vapor concentration [24].

The DVE-LS method for measuring soil water isotopes employs numerous, non-uniform correction methods. Currently, the correction methods can be mainly classified into three categories. The first category considers only the fractionation coefficient between liquid water and water vapor, using isotopically enriched liquid water as the standard sample [21,25–27]. The second category uses liquid water with known isotopic values that is added to the soil and dried, before being rehydrated to the same moisture content as the standard sample. Therefore, this method, unlike the first correction method, also takes into account the impact of soil texture type on the measured isotopic value [8,28–30].

The third method uses soil samples of different textures that are dried and rehydrated to different moisture contents from the standard sample. Unlike the second method, the third method also considers the influence of soil moisture content [31]. Rothfuss et al. (2013) found that equilibrium temperature significantly affected the water isotope fractionation in sandy soil when using the DVE method to measure soil water isotope composition [32]. However, no report has been published on the influence of equilibrium temperature on DVE-LS-determined soil water isotopes and the correction method related to different soil textures. Nevertheless, to obtain more accurate soil water isotope information, a systematic experiment is needed to investigate the influence of different factors on isotope deviations and establish correction methods.

Therefore, this study focuses on the deviation in soil water isotopes caused by equilibrium temperature: (1) after rehydrating dried soil in experiments, the effect of soil texture and moisture content on DVE-LS-determined soil water fractionation at various equilibrium temperatures was studied, and correction equations for isotopic deviation and the factors affecting it were built; (2) the correction equation was used to correct the measured values of the DVE-LS method at different equilibrium temperatures through field soil experiments. The corrected values were compared with the measured values of the CVD method, and the correction equation established in (1) was verified to improve the accuracy of the DVE-LS measurement of soil water isotopes. This study offers valuable guidance for enhancing the preparation of DVE-LS applications in the field and facilitating in situ and long-term series-based soil water isotope monitoring.

2. Materials and Methods

2.1. Soil Sample Preparation and Indicator Determination

2.1.1. Soil-Drying and Rehydration Test

A total of five soils with different textures were used in the indoor experiment, four of which were field-sampled (Yangling, Shaanxi (ST), Haibara, Shaanxi (HY), Changwu, Shaanxi (CW), and Weinan, Shaanxi (WN), and one was purchased as a commercially available soil mixture (PZ). Soil texture (Table 1), soil water content, and basic soil physicochemical properties (Table 2) were determined separately. The soil was packed into glass jars and dried in an oven until it reached equilibrium weight. We then added water samples with known isotopic content (Table 3) to dry soil to prepare soil samples with volumetric soil moisture contents of 5%, 10%, 20%, and 30%, respectively. Afterward, these soil samples were sealed and left to equilibrate for 10 days at temperatures of 4.89 °C, 17.41 °C, 23.35 °C, 29.67 °C and 36.43 °C. Three replicates were set up for each experimental treatment, a total of 300 samples. These samples were used to establish and calibrate the calibration equations.

Table 1. Soil collection location, soil type, texture composition, and moisture content after air drying.

Sample Number	Sampling Site	Soil Type	Clay Content (g g^{-1})	Silt Content (g g^{-1})	Sand Content (g g^{-1})	Water Content (g g^{-1})
ST	Yangling	Sandy soil	0.01	0.03	0.96	0.00
HY	Haiyuan	Silty loam soil	0.13	0.57	0.30	0.01
CW	Changwu	Silty loam soil	0.23	0.65	0.12	0.03
WN	Weinan	Silty clay loam	0.33	0.62	0.05	0.04
PZ	Commercial Mixed soil	Silty clay	0.45	0.51	0.04	0.06

Table 2. Soil characteristics of the soil for the test.

Parameter	ST	HY	CW	WN	PZ
pH	9.4	9.4	8.7	8.8	8.4
Organic carbon (g kg^{-1})	3.6	5.6	7.8	3.5	7.8
Cation exchange capacity (m eq 100 g^{-1})	11.7	15.6	12.2	11.28	13.3

Table 3. Information on the water sample for the test.

Water Sample	Water Source Type	Water Source Location	δ2H (‰)	δ18O (‰)
SWS1	Seawater	Yantai	−11.36	−1.33
SWS2	Snow water	Xizang	−103.85	−14.18
SWS3	Ultrapure water	-	−61.86	−9.45
WS1	Nongfu Spring mineral water	Changbai Mountain	−93.81	−13.24
WS2	Ganten	Chengdu	−58.82	−8.56
WS3	Watsons	Dongguan	−33.33	−4.59

2.1.2. Field Soil Test

The field soil samples were taken from Wangdong Village, Changwu County, Shaanxi Province, and the Xindiangou watershed, Suide County, Shaanxi Province. Soil samples were depths of taken at 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, and 6.0 m from a field in Wangdong Village, respectively. Soil samples were also taken at depths of 0.6, 1.2, 1.8, 2.4, 3.0, 4.2, 5.4, 6.6, 7.8, 9.0, 10.2, 11.4, 12.6, 13.8, and 15.0 m from a 15 m soil profile in the Xindian Ditch watershed. Each soil sample was mixed well and divided into two parts. One part was placed in an aluminum box to determine the water content and the other part was sealed and refrigerated to determine its isotopic composition. A portion of the sealed and refrigerated soil was equilibrated at 4.89 °C, 23.35 °C, and 36.43 °C for 10 days to determine the isotopes of soil moisture, using the DVE-LS method. The other part of the sealed and refrigerated soil was used to determine the isotopes of soil moisture using the CVD method. The isotope values of soil water measured by the CVD method were used as a reference to verify whether the DVE-LS method of measurement, corrected using the calibration method, was able to reduce the error.

2.2. Preparation of Standard and Accession Water Samples

Standard water samples 1 and 2 were used as standard samples during the sampling process to calibrate the measured water vapor isotope values to liquid water isotope values. Water sample 2 was used as a quality control standard sample to detect water loss from the studied sample during equilibration. Accession water samples 1 and 3 were added to those soil samples with known isotope values. Before they were used, accession water samples 1 and 3 were deionized using an ultrapure water machine, to make sure that the water added to the soil was of the same quality as the standard water samples. The water samples were isotopically determined using a liquid water laser isotope analyzer (LGR IWA-45EP, Los Gatos Research Inc., San Jose, CA, USA).

2.3. Isotope Measurements of Soil Drying and Rehydration and Field Soils Samples

2.3.1. Soil Water Isotope Measurement Process by DVE-LS

Soil water isotope and field soil isotope measurements in the soil drying and rehydration test were made using the DVE-LS. Equilibrated soil samples were taken and the soil water isotopes in the samples were measured using portable water isotope analyzers (GLA132 Series UItraportable Analyzers, Zurich, Swiss Confederation). In order to ensure

the reliability of the measurement results using the DVE-LS method, the accuracy of the instrument needs to be determined. In this study, the precision of the instrument was established by determining the root mean square error (RMSE) of the deviation of δ^2H and δ^{18}O from the reference water isotope (Table 3) for water sample SW1, based on the DVE-LS method, using a portable water isotope analyzer. The RMSE of the deviation of δ^2H and δ^{18}O from the reference water isotope was measured by repeating the measurement process 15 times, which yielded 2.34‰ and 0.42‰, respectively. Therefore, the accuracy of the portable water isotope analyzer for the determination of liquid water was obtained as δ^2H: ±2.34‰ ± 0.4 and δ^{18}O: ±0.42‰ ± 0.14, respectively.

2.3.2. Process of the CVD Extraction of Field Soil Water

Field soil water isotopes were extracted from the samples using CVD, and their isotopic values were determined using LGR. The LGR system for determining their isotopes was self-assembled, according to the method used by Koeniger et al. (2011) [33]. This system consists of three main components: evaporation–condensation, evacuation, and heating. The evaporation–condensation section uses a pair of 12 mL headspace bottles to replace the original sample and uses collection bottles for more efficient condensation. A stainless-steel capillary tube with a diameter of 1.56 mm is used to connect the sample and collection bottles to form a complete extraction system. Headspace bottles are a common container for storing and transporting gas samples; the gas tightness has been extensively tested and verified [34] and they are relatively inexpensive. For better vacuum extraction, a TRP-12 (220 V) model vacuum pump was used. A temperature-adjustable metal bath was used for the heating component, and an aluminum metal module with 3 × 4 holes (10 mm diameter and 80 mm depth) was placed in the oil bath to achieve stability for the extraction experiments. The collection bottle was sealed immediately after the extraction was completed. The extracted water samples were stored in a refrigerator at 4 °C, pending measurement of their isotopic values. All samples were weighed before and after extraction, and the extraction efficiency was calculated after drying in an oven at 105 °C for 24 h. When the extraction efficiency was greater than 98%, this indicated that the sample's extraction operation was qualified [35].

2.4. Data Analysis

2.4.1. Calibration Method

Portable water isotope analyzers need to be calibrated, due to the effects of instrument drift. The usual method is to use the instrument to measure a standard water sample because the isotopic values of δ^2H and δ^{18}O of the standard water sample are known; by establishing a calibration curve (Equation (1)) using the measured values and the true values, the effect of instrument drift on the measured values is eliminated, making the results of the measurements closer to the true values. The standard water samples that are used need to be processed under the same equilibrium temperature conditions as the soil samples to be measured; the standard water samples were chosen to be the more flattened water sample SWS1 and the more enriched water sample SWS2, with the aim of ensuring that the isotopic values of the measured samples were all in the range of those of the standard water samples. At each equilibrium temperature, after each measurement of δ^2H and δ^{18}O for a textured soil (Table 1), the δ^2H and δ^{18}O values of water sample SWS1 and water sample SWS2 were measured four times:

$$\delta_{Std\text{-}L} = a \times \delta_{Std\text{-}V} + b \quad (1)$$

where $\delta_{Std\text{-}V}$ and $\delta_{Std\text{-}L}$ are the water vapor measurements of the standard samples and the true value of liquid water, respectively, and a and b are the linear regression fitting parameters, respectively.

Definition of the soil water isotope deviations ($\Delta\delta$, ‰) used the isotope values of the added water samples or CVDs as a reference frame:

$$\Delta\delta = \delta_m - \delta_n \tag{2}$$

where δ_m and δ_n are the measured liquid values and added water isotope values or CVD measurements, respectively. A paired t-test was used to determine whether the difference between the two sets of data was significant:

$$t = \frac{\overline{x} - \overline{y}}{\sqrt{\sigma_x^2 + \sigma_y^2}} \tag{3}$$

where $\overline{x}$ and $\overline{y}$ are the means of the variables x and y, respectively, and σ_x and σ_y are the standard errors of x and y, respectively; $t > 1.96$ or $p < 0.05$ indicates a significant difference.

2.4.2. Linear Regression Modeling Steps

Because of the significant effect of water vapor concentration on isotope values, unqualified samples in which the water vapor concentration during the sampling process was not found to be between the water vapor concentrations of the two standard water samples were excluded from the raw data, and 270 soil sample data points were finally obtained. The 270 soil samples were divided into two groups; one group of 216 samples was used to establish the calibration model, and the remaining 54 samples were used to validate the established calibration function. Simple multiple linear regression in SPSS was used for data processing in this part of the experiment, to establish quantitative relationships between the isotope deviation values ($\Delta\delta^2$H or $\Delta\delta^{18}$O) and equilibrium temperature, soil clay content, and water content. The general equation was as follows:

$$y = \hat{y} + \varepsilon = a_0 + \sum_{i=1}^{n} a_i x_i + \varepsilon \tag{4}$$

where y and $\hat{y}$ are the measured and predicted variables, respectively, ε is the error term, a_0 is the equation intercept, a_i is the regression coefficient, and x_i denotes the i independent variable, i = 1, 2, 3, …; n is the number of independent variables in the regression equation, n = 1, 2, 3.

$$\Delta\delta^2 H = a_0 + a_1 \cdot SCC + a_2 \cdot SWC + a_3 \cdot SCC \times SWC + a_4 \cdot ET \tag{5}$$

Here, SWC is soil water content (g g^{-1}), SCC is soil clay content (g g^{-1}), $SCC \times SWC$ is the interaction between SCC and SWC, and ET is the equilibrium temperature (°C).

$$\delta^2 H_{Correction} = \delta^2 H_{Measurement} - \Delta\delta^2 H \tag{6}$$

Represents isotope values before and after calibration $\delta^2 H_{Measurement}$ and $\delta^2 H_{Correction}$ represents isotope values before and after calibration.

2.4.3. Model Evaluation

The predictive performance of the calibration function is assessed by three metrics, namely, the R^2, the adjusted R^2 (*Adj-*R^2), and the root mean square error (RMSE):

$$R^2 = \frac{[\mathrm{cov}(\hat{y}_i, y_i]^2}{\mathrm{var}(\hat{y}_i)\mathrm{var}(y_i)} \tag{7}$$

$$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(y_i - \hat{y}_i)^2} \tag{8}$$

$$Adj\text{-}\mathrm{R}^2 = 1 - \frac{\left(1 - \mathrm{R}^2\right)(n-1)}{n-p-1} \tag{9}$$

where y_i and $\hat{y}_i$ represent the first measured and predicted values, respectively, and where n =1, 2, …, n. n and p represent the number of samples and the number of variables, respectively. Adjusted R^2 (*Adj-*R^2) is the corrected version of R^2 after taking into account the number of predictor variables, which not only reflects the predictive power of the model but also expresses the percentage of total variance explained by the predictions; the RMSE is used in the model to assess the standard deviation of the overall error in the predictions. A good model has a small RMSE value and a relatively high *Adj-*R^2. *Adj-*R^2 is the coefficient of determination of the modification after accounting for the number of predictions, which characterizes the predictive ability of the model; the closer *Adj-*R^2 is to 1, the stronger the predictive ability.

2.4.4. Statistical Analyses

The experimental data in this section were processed using SPSS software (IBM SPSS Statistics, Version 20). A multifactor ANOVA was used to compare the effects of equilibrium temperature, clay grain content, and water content on the isotope deviation values, followed by a simple stepwise multiple linear regression analysis to determine the significantly influential factors and to establish a correction equation between Δδ and the influencing factors. Differences between means were compared using *t*-tests, and when t > 1.96 ($p < 0.05$) indicated that the differences were statistically significant, the related graphs were plotted using Origin 2022 b software.

3. Results and Discussion

3.1. The Stability of the Instrument at Different Equilibrium Temperatures

Before performing the experiment, the portable water isotope analyzer was tested to see how stable it was in different settings. The isotope values of the SWS3, WS1, WS2, and WS3 water samples were found using the instrument at 4.89 °C, 23.35 °C, and 36.43 °C. The isotopic information for the water samples is presented in Table 3. The results show that the measured values deviate from the reference water values (calculated by Equation (2)) in decreasing order from low to high at the three equilibrium temperatures, namely, -1.97 ± 1.4‰ to 1.1 ± 2.04‰, -2.06 ± 0.38‰ to 1.42 ± 0.41‰, and -1.81 ± 0.98‰ to 0.25 ± 0.08‰ (Figure 1). However, the differences between the measured values and the true values for both the relatively enriched and depleted water samples were less than the precision range set by the instrument: δ^2H < 2.34‰, δ^{18}O < 0.42‰. A significance test was also performed between each measured water sample and the reference water sample at three different equilibrium temperatures (Figure 1). No significant differences were found between the measured results of the four different water samples at those equilibrium temperatures and the true values of the liquid water. This indicates that the instrument

is stable and reliable for measuring within the equilibrium temperature range of 5 °C to 36 °C.

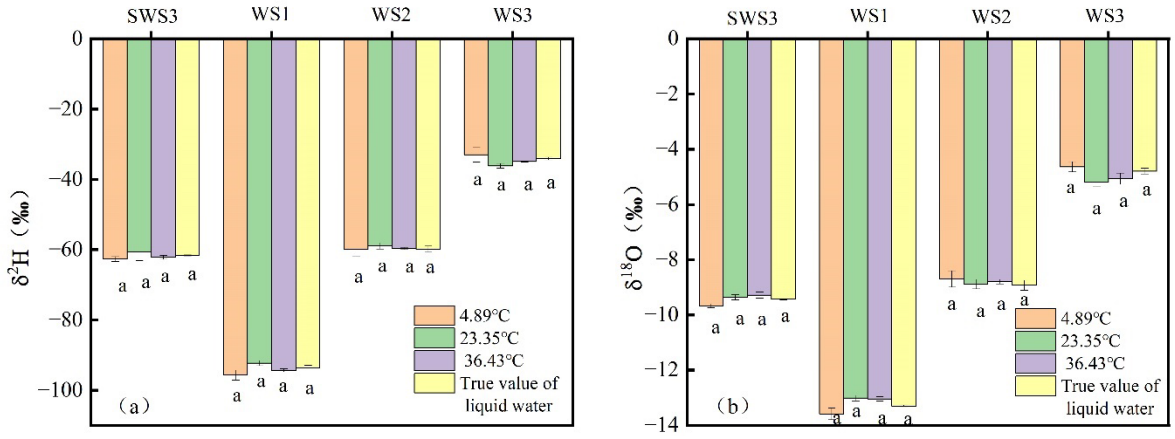


Figure 1. Comparison between the measured values of the different water samples and the true values of liquid water at different equilibrium temperatures for δ^2H (**a**) and δ^{18}O (**b**), as measured by a portable water isotope analyzer. Different lowercase letters indicate a significant difference ($p < 0.05$), and the same letters indicate no significant difference ($p < 0.05$).

3.2. Effect of Equilibrium Temperature on Isotopic Deviation Values

DVE-LS checks how far soil water isotopes are from the reference isotopes ($\Delta\delta^2$H and $\Delta\delta^{18}$O, determined in Equation (2)), taking into account the amount of clay and moisture in the soil at various equilibrium temperatures. At the same equilibrium temperature, the deviation of $\Delta\delta^2$H and $\Delta\delta^{18}$O increases with increasing clay content. For soil with a clay content of 0.05 g g^{-1}, the maximum values of $\Delta\delta^2$H and $\Delta\delta^{18}$O are 0.07 ± 1.32‰ and −0.21 ± 0.17‰; for soil with a clay content of 0.45 g g^{-1}, the maximum values of $\Delta\delta^2$H and $\Delta\delta^{18}$O are 13.95 ± 0.39‰ and 1.71 ± 0.19‰. The $\Delta\delta^2$H of the sample with an SCC of 0.23 g g^{-1}, 0.33 g g^{-1}, and 0.45 g g^{-1} and an SWC of 0.05 g g^{-1}, 0.10 g g^{-1}, and 0.20 g g^{-1} is beyond the accuracy range of the instrument at all five equilibrium temperatures. Only the fraction of $\Delta\delta^{18}$O with an SWC of 0.05 g g^{-1} and 0.10 g g^{-1} is out of the accuracy range of the instrument (Figure 2). The water measured by DVE-LS was vaporized soil water, and the isotopic value of the vaporized water determines the isotopic value of the water in the soil [36]. During the vaporization of soil water in the container, lighter water molecules are preferentially adsorbed by soil particles [37]. A portion of the free water that is not bound by the soil evaporates directly into the top space, while another portion is adsorbed on the surface of the soil particles. The water that is bound by the soil requires more energy to evaporate [38]. The binding force of soil on water is related to soil texture; the higher the clay content, the greater the binding force, and the more difficult it is for water to vaporize [38]. Therefore, when using DVE-LS to measure the isotopic value of soil water with a high clay content, a large isotopic deviation occurs, and the deviation effect increases with the increase in soil clay content. In their study on the adsorption of water molecules by clay in the soil, Orlowski et al. (2016) and Pratt et al. (2015) also found similar results [39,40]. They pointed out that the clay content of the soil is one of the main reasons for the significant deviation of DVE-LS in measuring soil water isotopes [23]. Conversely, soils may have the ability to change the distribution of water isotopes in small and large pores [30]. As shown by the water vapor balance, soil particles take in more of the water that has been lost from larger pores and release it into smaller pores. This makes the larger pores more isotopically rich and the smaller pores less isotopically rich [38].

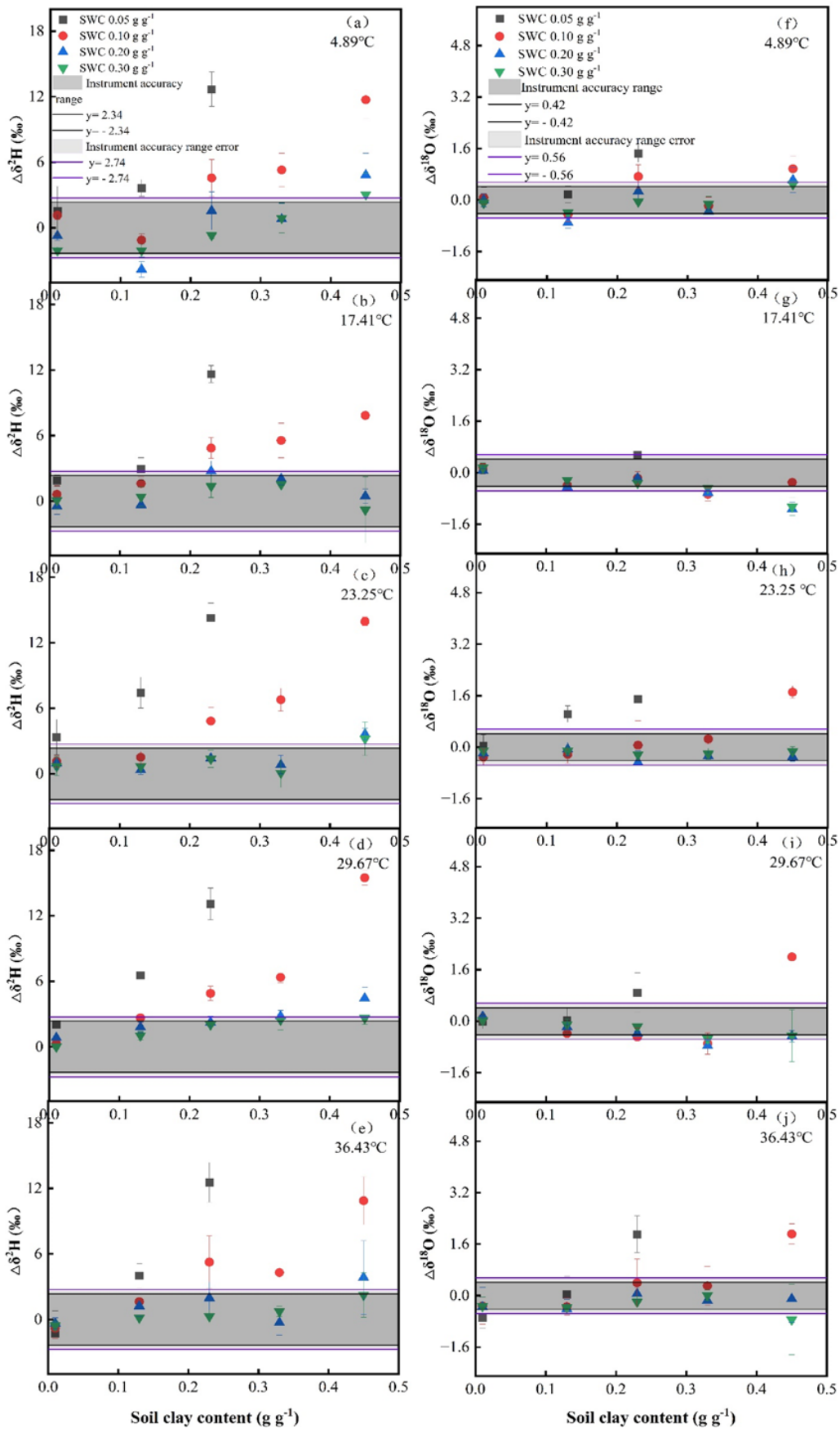


Figure 2. Variation trend of the soil water isotope deviation values for $\Delta\delta^2H$ (**a**–**e**) and $\Delta\delta^{18}O$ (**f**–**j**) with the soil clay content and soil water content under different equilibrium temperatures.

At the same equilibrium temperature, $\Delta\delta^2H$ and $\Delta\delta^{18}O$ decreased with increasing water content, and the isotopic deviation values gradually decreased to vary within the range of zero. For the same type of soil, the deviations were smallest when the soil contained 0.30 g g^{-3} of water, with $\Delta\delta^2H = 0.07 \pm 1.32‰$ and $\Delta\delta^{18}O = -0.21 \pm 0.17‰$. When the water content was lowered to 0.05 g g^{-2}, the deviations of $\Delta\delta^2H$ and $\Delta\delta^{18}O$ were the highest, at $14.26 \pm 1.36‰$ and $1.49 \pm 0.84‰$, respectively. Meanwhile, the soil with a water content of 0.05 g g^{-1} showed the largest dispersion of deviation values. Except for soils with clay contents of 0.01 g g^{-1} and 0.13 g g^{-1}, soils with a water content of 0.10 g g^{-1} did not alter the overall trend of water content in terms of isotope deviation values, despite exhibiting distinct dispersion phenomena. At soil moisture contents of 0.20 g g^{-1} and 0.30 g g^{-1}, there were no significant differences in isotopic deviation for any of the five textures used in the experiment. At different equilibrium temperatures, the mean values of $\Delta\delta^2H$ and $\Delta\delta^{18}O$ were 4.89 °C < 17.41 °C < 36.43 °C < 23.25 °C < 29.67 °C and 17.41 °C > 4.89 °C > 23.25 °C > 29.67 °C > 36.43 °C, respectively. On the whole, $\Delta\delta^2H$ increases with increasing temperature, while $\Delta\delta^{18}O$ shows the opposite trend (Figure 2). Specifically, the effects of clay content and water content on soil water isotope deviation at different equilibrium temperatures are different. The reason for these results is mainly due to the fact that the amount of water present in the soil pore space after the water from the low SWC treatment (0.05 g g^{-1}) is adsorbed by the soil particles is relatively small compared to that in the high SWC treatment. However, the DVE-LS method mainly determines the evaporated liquid water from the soil pores because the DVE-LS method does not evaporate water adsorbed by the soil particles from the soil, due to its low temperature [12]. Soils with low SWC evaporate less water from the soil pore space, resulting in a lower concentration of water molecules in the soil in the headspace of the container, which causes the deviation values to be greater for soils with low SWC than for soils with high SWC [31,41].

3.3. Correction Equation for Isotope Deviation, Based on Equilibrium Temperature, Soil Clay Content, and Soil Water Content

The effects of equilibrium temperature, soil clay content, soil water content, and the interaction of clay content and water content on the soil water isotope bias of DVE-LS measurements were analyzed with a multifactor ANOVA, which showed that equilibrium temperature, soil clay content, soil water content, and the interaction of clay content and water content all had a significant effect on $\Delta\delta^2H$, whereas only the soil water content had a significant effect on $\Delta\delta^{18}O$, while none of the other factors produced significant effects (Table 4). Therefore, correction equations based on the three factors of equilibrium temperature, soil clay content, and soil water content on isotopic bias were established for $\Delta\delta^2H$ only. The effects of equilibrium temperature, soil clay content, and the interaction of soil clay content and soil water content on $\Delta\delta^{18}O$ were not significant; therefore, correction equations based on the three factors of equilibrium temperature, soil clay content, and soil water content on isotope bias were not established for $\Delta\delta^{18}O$.

With the help of the training data set and those factors that had a major impact on $\Delta\delta^2H$ as predictors, a predictive function for $\Delta\delta^2H$ was created using Equations (5) and (6). The predictive performance metrics for all predictive equations are shown in Table 5. The adjusted R^2 of the $\Delta\delta^2H$ prediction model was 0.67, indicating that the factors explain 67% of the total variance of $\Delta\delta^2H$. We used validation data sets to check how well the prediction worked. The RMSE of the measurement results went from 4.53‰ to 2.50‰ before and after calibration, which was close to the instrument's measurement accuracy range (δ^2H: $2.34 \pm 0.4‰$) (Table 5). The performance of the predicted equations was evaluated using the validation dataset. As can be seen in Figure 3, the scatter points of the training dataset are clustered on the 1:1 line between the measured and simulation values of $\Delta\delta^2H$, and

most of the points lie within the instrumental accuracy range (the shaded part), indicating accurate and stable prediction performance.

Table 4. Effects of equilibrium temperature, soil clay content, and water content on the soil water isotope $\Delta\delta^2H$ and $\Delta\delta^{18}O$ analysis of variance of the results concerning impact.

Variable	*p* Value	
	$\Delta\delta^2H$	$\Delta\delta^{18}O$
Equilibrium temperature	<0.05	>0.05
Soil clay content	<0.05	>0.05
Soil water content	<0.05	<0.05
Soil clay content × Soil water content	<0.05	>0.05
Intercept	>0.05	<0.05

Note: The training data were measured at 4.89 °C, 23.35 °C, 17.41 °C, and 29.67 °C, while the verification data were measured at 36.43 °C. RMSE (‰) was calculated using the isotopic values and reference water isotopic values before and after correction.

Table 5. Isotope bias ($\Delta\delta^2H$ and $\Delta\delta^{18}O$) regression coefficients and predictive performance indicators of the ^{18}O correction equation.

Data Sets	Model	a_0	a_1	a_2	a_3	a_4	*Adj*-R^2	RMSE (‰)
Training data	$\Delta\delta^2H$	0.60 ± 1.12	29.93 ± 4.2	−10.96 ± 5.83	−82.88 ± 19.6	0.07 ± 0.03	0.67	
	p	0.53 (removed)	<0.05	<0.05	<0.05	<0.05		
Validating data	Before correction							4.53
	After correction							2.50

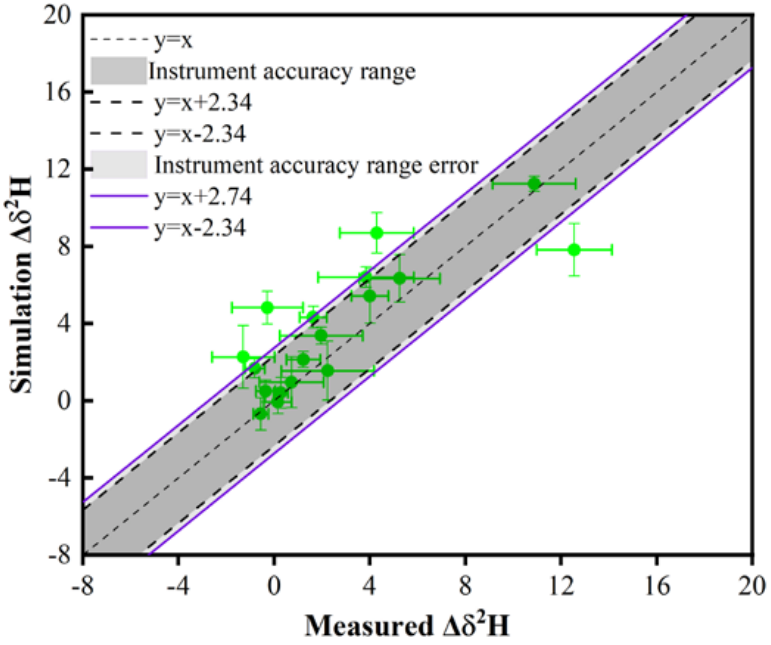


Figure 3. Validation dataset (δ^2H) scatter plot of simulation deviation and measured deviation.

3.4. Application of Correction Equations Under Different Equilibrium Temperature Conditions

Under different equilibrium temperature conditions, the following three methods were used to verify the calibration of soil water isotopes measured by DVE-LS.

Correction Equation (1): Following the measurement of four soil samples, the cyclic measurement of standard water samples 1 and 2 (Table 3) transformed the gaseous value of the measured soil water isotope into a liquid value using the standard water sample.

Correction Equation (2): y = x + a, where x is the water isotope value obtained by water vapor equilibrium 1, and a represents the difference between the measured soil water isotope and the reference liquid water isotope. This difference was obtained by matching the texture and water content of the soil in the laboratory test with that in the field test.

Correction Equation (3): We calculated the model equilibrium temperature, water content, and clay content with isotopic deviation values using Equations (7)–(9) above.

The average water content and clay content of soil in the Changwu field were 0.18 g g^{-1} and 0.18 g g^{-1}, respectively. The average field soil water content in Suide was 0.05 g g^{-1}, and the average clay content was 0.10 g g^{-1} (Figure 4). The soil water isotope values in the Changwu and Suide regions were measured using DVE-LS. The measured values were then corrected, using the three correction equations listed above. The RMSE was calculated by comparing the RMSE values before and after each correction method to the CVD measurement results (Table 6). The results show that the corrected DVE-LS measured values and the CVD measured values show the same variation trend as found with the soil depth. In both regions, more hydrogen isotopes were enriched than with the CVD method (Figure 5). In two regions and at three equilibrium temperatures, the correction effect of model 3 is the best, followed by model 2, and the correction effect of model 1 is the worst.

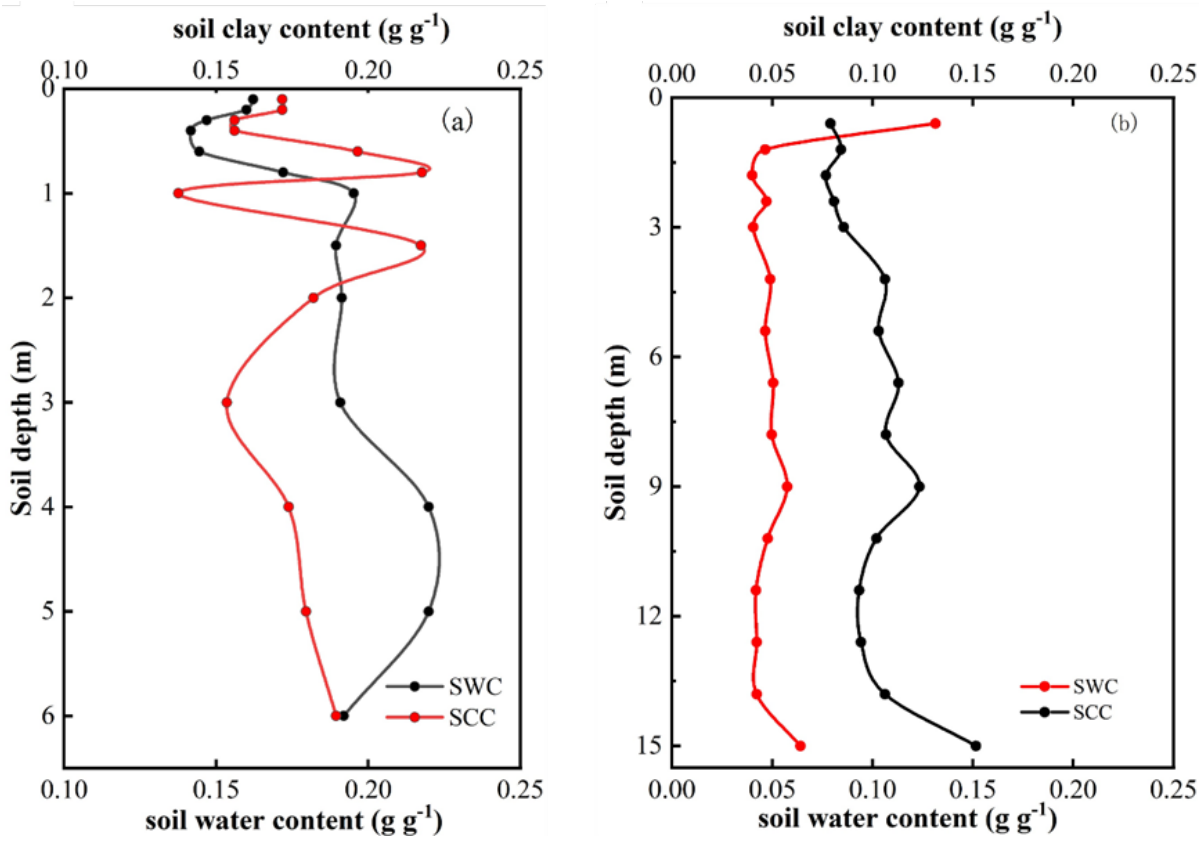


Figure 4. Soil water content and soil clay content of the Changwu (**a**) and Suide (**b**) deep profiles.

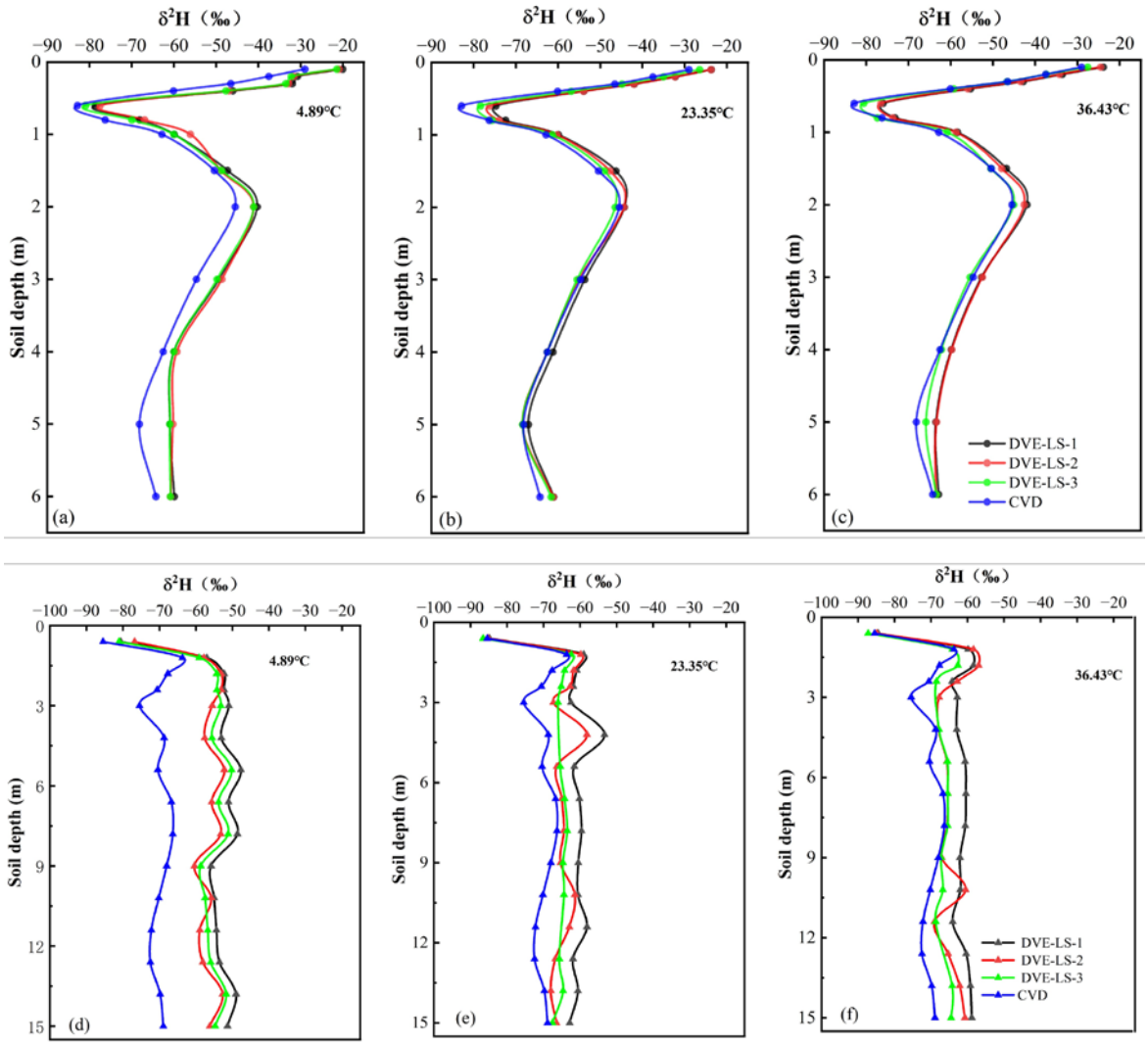


Figure 5. Under different equilibrium temperatures for DVE-LS correction, using different methods and vacuum extraction in the Changwu deep profile (**a**–**c**) and Suide deep profile (**d**–**f**), of soil water isotope $\Delta\delta^2H$ distribution.

Although the RMSE of water vapor balance 3 is lower than that of water vapor balance 1 and water vapor balance 2, the RMSE of the soil equilibrium under a low equilibrium temperature (4.89 °C) is still higher than that using the CVD method (Changwu δ^2H: 6.67‰; Suide δ^2H: 13.66‰) (Figure 5). The RMSE of the soil samples in Changwu at normal temperatures (23.35 °C) and high temperatures (36.43 °C) was measured at 2.14‰ and 1.24‰, compared to the results from CVD. These values were within the accuracy range of the instrument (δ^2H: 2.34 ± 0.4‰), and, as the equilibrium temperature rises, the results become more similar to those from vacuum extraction. By comparing the measured results of soil samples in Suide at a normal equilibrium temperatures (23.35 °C) and a high equilibrium temperature (36.43 °C), we can see that the RMSE is 4.73‰ for a normal equilibrium temperature and 4.14 °C for a high equilibrium temperature. This also shows that as the equilibrium temperature rises, the results become more similar to those of CVD. However, all of these are beyond the accuracy range of the instrument (δ^2H: 2.34 ± 0.4‰) (Figure 5). The main reason for the above results is that because DVE-LS measures soil water isotopes, the minimum soil water content required is 0.05 g g^{-1} [12,21]. The minimum water content of the Changwu field soil is 0.12 g g^{-1}, although it is much higher than the minimum water content of 0.05 g g^{-1} required by DVE-LS. We found that the average amount of water in Suide is 0.05 g g^{-1}, and the amount of water below 0.6 m gradually

becomes less than 0.05 g g^{-1}. This is much lower than the amount of water needed for the DVE-LS method and could explain the difference that was recorded [21,42]. As a result, the RMSE values fall outside the accuracy range of the instrument. When DVE-LS was used to determine the soil water isotopes, the water vapor concentration in the top space of the container was insufficient, resulting in a large deviation in the measurement results [12,43]. Therefore, it is not recommended to use DVE-LS to measure soil isotopes when the soil water content is less than 0.05 g g^{-1}.

Table 6. RMSE (‰) between the isotope values of different correction methods applied to wet soil in the Changwu and Suide fields and with vacuum extraction.

Soil Sample	Equilibrium Temperature (°C)	Correction Method	RMSE (‰)
Changwu wet soil	4.89	Correction Equation (1)	7.71
		Correction Equation (2)	7.67
		Correction Equation (3)	6.67
	23.35	Correction Equation (1)	4.29
		Correction Equation (2)	3.81
		Correction Equation (3)	2.14
	36.43	Correction Equation (1)	4.07
		Correction Equation (2)	3.64
		Correction Equation (3)	1.24
Suide soil	4.89	Correction Equation (1)	18.37
		Correction Equation (2)	13.85
		Correction Equation (3)	13.66
	23.35	Correction Equation (1)	10.23
		Correction Equation (2)	5.91
		Correction Equation (3)	4.73
	36.43	Correction Equation (1)	8.99
		Correction Equation (2)	6.16
		Correction Equation (3)	4.14

The DVE-LS method is significantly affected by the equilibrium temperature when measuring soil water isotopes. The water vapor balance correction model that was created through laboratory tests at five different equilibrium temperatures can effectively lower the deviation from CVD, especially when the equilibrium temperature is normal or high. The RMSE difference between the two is 1.24‰ (Figure 5). This is mainly because soil water isotope fractionation shows a similar trend to pure liquid water fractionation, which decreases with the increase in equilibrium temperature, except that soil water fractionation is affected by its physical and chemical properties [31]. All three correction models show that the correction effect increases with the increase in equilibrium temperature. At low equilibrium temperatures, the correction effect is at its worst. The main reason for this is that at low equilibrium temperatures, water molecules in the soil diffuse slowly to the top space, and the soil particles also adsorb lighter water molecules. Lighter water molecules in the water vapor in the top space are relatively fewer than the heavy water molecules, resulting in the enrichment of Correction Equation (1) compared with normal and high equilibrium temperatures. The δ^2H deviation value increases. However, correction equation (2) and correction equation (3) are built on the basis of correction equation (1), so that when the deviation of correction equation (1) is too large, even if correction equation (2) and correction equation (3) add other influencing factors to the correction equation, it is difficult to achieve satisfactory accuracy.

4. Conclusions

The results indicate that $\Delta\delta^2H$ decreases as the equilibrium temperature and soil water content increase, and $\Delta\delta^2H$ rises with the increase in soil clay content. The equilibrium temperature has a significant impact on $\Delta\delta^2H$ but not on $\Delta\delta^{18}O$. Hence, a correction equation based on equilibrium temperature ($R^2 = 0.67$) is established solely for $\Delta\delta^2H$. Field experiments were carried out to validate the correction equation. It was discovered that the third correction equation, which was founded on equilibrium temperature, performed optimally for DVE-LS measurements of soil isotope values in Changwu. The RMSE decreased from 4.07‰ to 1.24‰, demonstrating that creating a correction model based on equilibrium temperature can enhance the accuracy of DVE-LS significantly. In conclusion, it is suggested that when using the DVE-LS method to measure soil water isotopes, the influence of equilibrium temperature should be incorporated into the correction equation, and, to minimize the deviation, the relative soil water content should be maintained above 5%; the application of this method should be avoided under low-temperature conditions.

Author Contributions: Conceptualization, R.H. and X.L. (Xiaoqing Liu); Methodology, R.H., J.F., L.B. and M.Z.; Software, L.B.; Validation, L.B. and X.L. (Xuejia Li); Formal analysis, Z.X.; Investigation, G.L.; Resources, X.L. (Xuejia Li) and G.L.; Data curation, Z.X. and X.L. (Xiaoqing Liu); Writing—original draft, Z.X. and M.Z.; Writing—review & editing, Z.X. and M.Z.; Supervision, J.F.; Funding acquisition, Z.X. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Energy Group Technology Project (GJNY-20-112, E210100498); National Key Research and Development Plan (2023YFF1306002); China Postdoctoral Science Foundation (No. 2022M720535).

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: We are thankful for the constructive comments received from anonymous reviewers and the editors.

Conflicts of Interest: Authors Zhenguo Xing, Ruimin He, Xuejia Li, Xiaoqing Liu and Gang Liu were employed by the company China Energy Shendong Coal Group Co., Ltd.; authors Zhenguo Xing, Ruimin He, Jie Fang and Lu Bai were employed by the company China Energy Investment Group. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Gabriel, B. Hydrology: The diversified economics of soil water. *Nature* **2015**, *525*, 43–44.
2. Liu, Z.; Dreybrodt, W.; Wang, H. A new direction in effective accounting for the atmospheric CO_2 budget: Considering the combined action of carbonate dissolution, the global water cycle and photosynthetic uptake of DIC by aquatic organisms. *Earth Sci. Rev.* **2010**, *99*, 162–172. [CrossRef]
3. Dansgaard, W. The Abundance of O18in Atmospheric Water and Water Vapour. *Tellus* **1953**, *5*, 461–469. [CrossRef]
4. Wang, H.; Si, B.; Pratt, D.; Li, H.; Ma, X. Calibration method affects the measured δ2H and δ18O in soil water by direct H2Oliquid–H2Ovapour equilibration with laser spectroscopy. *Hydrol. Process.* **2019**, *34*, 506–516. [CrossRef]
5. Benjamin, G.; Barbara, H.; Markus, W. Technical note: Unresolved aspects of the direct vapor equilibration method for stable isotope analysis (δ18O, δ2H) of matrix-bound water: Unifying protocols through empirical and mathematical scrutiny. *Hydrol. Earth Syst. Sci.* **2021**, *25*, 5219–5235.
6. West, A.G.; Patrickson, S.J.; Ehleringer, J.R. Water extraction times for plant and soil materials used in stable isotope analysis. *Rapid Commun. Mass Spectrom. RCM* **2006**, *20*, 1317–1321. [CrossRef] [PubMed]
7. Figueroa-Johnson, M.A.; Tindall, J.A.; Friedel, M. A Comparison of 18Oδ Composition of Water Extracted from Suction Lysimeters, Centrifugation, and Azeotropic Distillation. *Water Air Soil Pollut.* **2007**, *184*, 63–75. [CrossRef]
8. Garvelmann, J.; Külls, C.; Weiler, M. A porewater-based stable isotope approach for the investigation of subsurface hydrological processes. *Hydrol. Earth Syst. Sci.* **2012**, *16*, 631–640. [CrossRef]
9. Kinga, R.; Peter, H.W. A method to extract soil water for stable isotope analysis. *J. Hydrol.* **1990**, *115*, 397–406. [CrossRef]

10. Adams, R.E.; Hyodo, A.; SantaMaria, T.; Wright, C.L.; Boutton, T.W.; West, J.B. Bound and mobile soil water isotope ratios are affected by soil texture and mineralogy, whereas extraction method influences their measurement. *Hydrol. Process.* **2020**, *34*, 991–1003. [CrossRef]
11. Bowers, W.H.; Mercer, J.J.; Pleasants, M.S.; Williams, D.G. A combination of soil water extraction methods quantifies the isotopic mixing of waters held at separate tensions in soil. *Hydrol. Earth Syst. Sci.* **2020**, *24*, 4045–4060.
12. Hendry, M.J.; Schmeling, E.; Wassenaar, L.I.; Barbour, S.L.; Pratt, D. Determining the stable isotope composition of pore water from saturated and unsaturated zone core: Improvements to the direct vapor equilibration laser spectroscopy method. *Hydrol. Earth Syst. Sci. Discuss.* **2015**, *12*, 6241–6274.
13. Tsuruta, K.; Yamamoto, H.; Katsuyama, M.; Kosugi, Y.; Okumura, M.; Matsuo, N. Effects of cryogenic vacuum distillation on the stable isotope ratios of soil water. *Hydrol. Res. Lett.* **2019**, *13*, 1–6. [CrossRef]
14. Deseano Diaz, P.; Nong, T.; Brüggemann, N.; Dubbert, M.; Javaux, M.; Orlowski, N.; Vereecken, H.; Rothfuss, Y. Insights into tension-mediated and antecedent water effects on soil water isotopic composition. *Vadose Zone J.* **2023**, *22*, e20288. [CrossRef]
15. Wang, H.; Yu, H.; He, D.; Li, M.; Si, B.; McDonnell, J.J.; Nehemy, M.F. Cryogenic vacuum distillation vs Cavitron methods in ecohydrology: Extraction protocol effects on plant water isotopic values. *J. Hydrol.* **2024**, *642*, 131853. [CrossRef]
16. Sprenger, M.; Tetzlaff, D.; Soulsby, C. Soil water stable isotopes reveal evaporation dynamics at the soil–plant–atmosphere interface of the critical zone. *Hydrol. Earth Syst. Sci.* **2017**, *21*, 3839–3858. [CrossRef]
17. Sodemann, Y.W.A.T.H. Correcting the impact of the isotope composition on the mixing ratio dependency of water vapour isotope measurements with cavity ring-down spectrometers. *Atmos. Meas. Tech.* **2020**, *13*, 3167–3190.
18. Vadibeler, D.; Stockinger, M.P.; Wassenaar, L.I.; Stumpp, C. Influence of equilibration time, soil texture, and saturation on the accuracy of porewater water isotope assays using the direct $H_2O_{(liquid)}$–$H_2O_{(vapor)}$ equilibration method. *J. Hydrol.* **2022**, *607*, 127560. [CrossRef]
19. Koehler, G.; Wassenaar, L.I.; Hendry, M.J. An automated technique for measuring deltaD and delta18O values of porewater by direct CO2 and H2 equilibration. *Anal. Chem.* **2000**, *72*, 5659–5664. [CrossRef]
20. Koeniger, P.; Gaj, M.; Beyer, M.; Himmelsbach, T.J.H.P. Review on soil water isotope-based groundwater recharge estimations. *Hydrol. Process.* **2016**, *30*, 2817–2834. [CrossRef]
21. Wassenaar, L.I.; Hendry, M.J.; Chostner, V.L.; Lis, G.P. High resolution pore water delta2H and delta18O measurements by H2O(liquid)-H2O(vapor) equilibration laser spectroscopy. *Environ. Sci. Technol.* **2008**, *42*, 9262–9267. [CrossRef]
22. Alexandra, M.; Florent, B.; Sophie, G.; Patrick, G.; Jean-François, H.; Guillaume, M. Improved accuracy and precision of water stable isotope measurements using the direct vapour equilibration method. *Rapid Commun. Mass Spectrom.* **2019**, *33*, 1613–1622.
23. Schmidt, M.; Maseyk, K.; Lett, C.; Biron, P.; Richard, P.; Bariac, T.; Seibt, U. Concentration effects on laser-based δ18O and δ2H measurements and implications for the calibration of vapour measurements with liquid standards. *Rapid Commun. Mass Spectrom.* **2010**, *24*, 3553–3561. [CrossRef]
24. Komiya, S.; Kondo, F.; Moossen, H.; Seifert, T.; Schultz, U.; Geilmann, H.; Walter, D.; Lavric, J.V. Characterizing water vapour concentration dependence of commercial cavity ring-down spectrometers for continuous on-site atmospheric water vapour isotope measurements in the tropics. *Atmos. Meas. Tech.* **2021**, *14*, 1439–1455. [CrossRef]
25. Hendry, M.J.; Barbour, S.L.; Novakowski, K.; Wassenaar, L.I. Paleohydrogeology of the Cretaceous sediments of the Williston Basin using stable isotopes of water. *Water Resour. Res.* **2013**, *49*, 4580–4592.
26. Barbour, S.L.; Hendry, M.J.; Carey, S.K. High-resolution profiling of the stable isotopes of water in unsaturated coal waste rock. *J. Hydrol.* **2016**, *534*, 616–629. [CrossRef]
27. David, K.; Timms, W.; Hughes, C.E.; Crawford, J.; McGeeney, D. Application of the pore water stable isotope method and hydrogeological approaches to characterise a wetland system. *Hydrol. Earth Syst. Sci.* **2018**, *22*, 6023–6041. [CrossRef]
28. Volkmann, T.H.M.; Weiler, M. Continual in situ monitoring of pore water stable isotopes in the subsurface. *Hydrol. Earth Syst. Sci.* **2014**, *18*, 1819–1833. [CrossRef]
29. Gaj, M.; Beyer, M.; Koeniger, P.; Wanke, H.; Hamutoko, J.; Himmelsbach, T. In situ unsaturated zone water stable isotope (2H and 18O) measurementsin semi-arid environments: A soil water balance. *Hydrol. Earth Syst. Sci.* **2016**, *20*, 715–731. [CrossRef]
30. Quade, M.; Klosterhalfen, A.; Graf, A.; Brüggemann, N.; Hermes, N.; Vereecken, H.; Rothfuss, Y. In-situ monitoring of soil water isotopic composition for partitioning of evapotranspiration during one growing season of sugar beet (*Beta vulgaris*). *Agric. For. Meteorol.* **2019**, *266–267*, 53–64. [CrossRef]
31. Oerter, E.J.; Bowen, G. In situ monitoring of H and O stable isotopes in soil water reveals ecohydrologic dynamics in managed soil systems. *Ecohydrology* **2017**, *10*, e1841. [CrossRef]
32. Rothfuss, Y.; Vereecken, H.; Brüggemann, N. Monitoring water stable isotopic composition in soils using gas-permeable tubing and infrared laser absorption spectroscopy. *Water Resour. Res.* **2013**, *49*, 3747–3755. [CrossRef]
33. Koeniger, P.; Marshall, J.D.; Link, T.; Mulch, A. An inexpensive, fast, and reliable method for vacuum extraction of soil and plant water for stable isotope analyses by mass spectrometry. *Rapid Commun. Mass Spectrom. RCM* **2011**, *25*, 3041–3048. [CrossRef] [PubMed]

34. Glatzel, S.; Well, R. Evaluation of septum-capped vials for storage of gas samples during air transport. *Environ. Monit. Assess.* **2008**, *136*, 307–311. [CrossRef]
35. Sprenger, M.; Herbstritt, B.; Weiler, M. Established methods and new opportunities for pore water stable isotope analysis. *Hydrol. Process.* **2015**, *29*, 5174–5192. [CrossRef]
36. Majoube, M. Fractionnement en oxygène 18 et en deutérium entre l'eau et sa vapeur. *J. Chim. Phys. Phys.-Chim. Biol.* **1971**, *68*, 1423–1436. [CrossRef]
37. Glen, R.W.; Peter, H.W.; Graham, B.A. Interlaboratory comparison of methods to determine the stable isotope composition of soil water. *Chem. Geol.* **1994**, *111*, 297–306. [CrossRef]
38. Gaj, M.; McDonnell, J.J. Possible soil tension controls on the isotopic equilibrium fractionation factor for evaporation from soil. *Hydrol. Process.* **2019**, *33*, 1629–1634. [CrossRef]
39. Orlowski, N.; Pratt, D.L.; McDonnell, J.J. Intercomparison of soil pore water extraction methods for stable isotope analysis. *Hydrol. Process.* **2016**, *30*, 3434–3449. [CrossRef]
40. Pratt, D.L.; Lu, M.; Lee Barbour, S.; Jim Hendry, M. An evaluation of materials and methods for vapour measurement of the isotopic composition of pore water in deep, unsaturated zones. *J. Isot. Environ. Health Stud.* **2016**, *52*, 529–543. [CrossRef] [PubMed]
41. Bowling, D.R.; Schulze, E.S.; Hall, S.J. Revisiting streamside trees that do not use stream water: Can the two water worlds hypothesis and snowpack isotopic effects explain a missing water source? *Ecohydrology* **2017**, *10*, e1771. [CrossRef]
42. Harrington, G.A.; Gardner, W.P.; Smerdon, B.D.; Hendry, M.J. Palaeohydrogeological insights from natural tracer profiles in aquitard porewater, Great Artesian Basin, Australia. *Water Resour. Res.* **2013**, *49*, 4054–4070.
43. Juske, H.; Kazimierz, R.; Shabtai, C. Isotope effects in the evaporation of water: A status report of the Craig-Gordon model. *Isot. Environ. Health Stud.* **2008**, *44*, 23–49.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.