

# Determining the Isotopic Composition of Surface Water Vapor Flux From High-Frequency Observations Using Flux-Gradient and the Keeling Methods

Yongbo Hu<sup>1</sup>, Wei Xiao<sup>1</sup>, Zhongwang Wei<sup>2</sup>, Lisa Welp<sup>3</sup>, Xuefa Wen<sup>4</sup>, and Xuhui Lee<sup>5</sup>

<sup>1</sup>Nanjing University of Information Science and Technology

<sup>2</sup>Yale University

<sup>3</sup>Purdue University

<sup>4</sup>Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences

<sup>5</sup>Yale University, School of Forestry and Environmental Studies

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## Abstract

The isotopic composition of surface water vapor flux ( $\delta$ ) is a quantity frequently used to investigate the local and regional water cycle. In this study, the  $\delta$  determined with the Keeling method was evaluated against the flux-gradient method and the Craig-Gordon model prediction. Previous studies have shown that the choice of regression fitting methods can bias the  $\delta$  intercept results and precision of the Keeling method. Here, the Keeling method was applied to high-frequency (0.2 to 1 Hz) data measured at a cropland and a lake site to test different regression methods. Results show that the Keeling method with the York's solution (YS) and the ordinary least squares (OLS) regression produced robust estimates of  $\delta$  when compared with the flux-gradient method. Increasing concentration range reduced the standard error of estimate but did not bring obvious improvement to the bias error for the YS and OLS regression. The Keeling result was better using data from two sampling heights than only one. There was evidence that the Keeling method with the OLS regression slightly outperformed the flux-gradient method during periods with small vertical vapor gradient. Results also show that the Keeling method with the geometric mean regression gave highly biased estimate of  $\delta$  for the types of isotope ratio infrared spectroscopy analyzer deployed in this study. These results can inform  $\delta$  calculations and future experimental designs.

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# **Determining the Isotopic Composition of Surface Water Vapor Flux From High-Frequency Observations Using Flux-Gradient and the Keeling Methods**

Yongbo Hu<sup>1,3</sup>, Wei Xiao<sup>1,3</sup>, Zhongwang Wei<sup>4</sup>, Lisa R. Welp<sup>5</sup>, Xuefa Wen<sup>6</sup>, Xuhui Lee<sup>2,1</sup>

<sup>1</sup>Yale-NUIST Center on Atmospheric Environment, International Joint Laboratory on Climate and Environment Change (ILCEC), Nanjing University of Information Science and Technology, Nanjing, China.

<sup>2</sup>School of Forestry and Environmental Studies, Yale University, New Haven, Connecticut, USA.

<sup>3</sup>NUIST-Wuxi Research Institute, Wuxi, China

<sup>4</sup>Department of Environmental Systems Science, ETH Zurich, Zürich, Switzerland

<sup>5</sup>Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, West Lafayette, Indiana, USA

<sup>6</sup>Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing, China.

Corresponding author: Xuhui Lee ([xuhui.lee@yale.edu](mailto:xuhui.lee@yale.edu))

## **Key Points:**

- High-frequency data was used with the Keeling method to calculate the <sup>18</sup>O isotopic composition of surface evaporation
- The Ordinary Least Squares and the York's Solution were appropriate regression methods for obtaining the Keeling intercept
- Under conditions of low vertical vapor concentration gradient, the Keeling method with OLS slightly outperformed the Flux-gradient method

**Abstract**

The isotopic composition of surface water vapor flux ( $\delta_E$ ) is a quantity frequently used to investigate the local and regional water cycle. In this study, the  $\delta_E$  determined with the Keeling method was evaluated against the flux-gradient method and the Craig-Gordon model prediction. Previous studies have shown that the choice of regression fitting methods can bias the  $\delta_E$  intercept results and precision of the Keeling method. Here, the Keeling method was applied to high-frequency (0.2 to 1 Hz) data measured at a cropland and a lake site to test different regression methods. Results show that the Keeling method with the York's solution (YS) and the ordinary least squares (OLS) regression produced robust estimates of  $\delta_E$  when compared with the flux-gradient method. Increasing concentration range reduced the standard error of estimate but did not bring obvious improvement to the bias error for the YS and OLS regression. The Keeling result was better using data from two sampling heights than only one. There was evidence that the Keeling method with the OLS regression slightly outperformed the flux-gradient method during periods with small vertical vapor gradient. Results also show that the Keeling method with the geometric mean regression gave highly biased estimate of  $\delta_E$  for the types of isotope ratio infrared spectroscopy analyzer deployed in this study. These results can inform  $\delta_E$  calculations and future experimental designs.

## 1 Introduction

The isotopic composition of surface water vapor flux ( $\delta_E$ ) is a key parameter in studies of the water cycle using isotopic tracer methods. It is used for estimating lake evaporation (Gibson et al., 1993; Xiao et al., 2017), constraining local moisture recycling (Bowen et al., 2019; Gat et al., 1994; Griffis et al., 2016; Wang et al., 2016; Xiao et al., 2018), characterizing sources of moisture in the atmospheric boundary layer (Lee et al., 2007; Simonin et al., 2014; Welp et al., 2008, 2012; Zannoni et al., 2019a), and partitioning of evapotranspiration in ecosystems (Good et al., 2014, 2015; Lu et al., 2017; Sun et al., 2019; Wei et al., 2018; Wen et al., 2016). Typically,  $\delta_E$  is determined with the Keeling plot method which is an application of a two-member mixing model. According to Keeling (1958), the intercept of the linear regression of the observed isotopic composition of water vapor,  $\delta_v$ , against the inverse of the water vapor concentration,  $1/c$ , is equivalent to  $\delta_E$ . The general form of this equation is

$$\delta_v = a + b(1/c) \quad (1)$$

where  $\delta_E = a$ .

An implicit assumption inherit in the Keeling method is that the isotopic signature of the surface water source should remain constant during the observational period. In field applications, the data used in the regression analysis are generally collected over a period of several hours (Delattre et al., 2015; Yepez et al., 2003, 2005; Zannoni et al., 2019b). However, temporal changes in atmospheric forcings, such as relative humidity and cloudiness, can result in large short-term (minutes to hours) fluctuations in  $\delta_E$  of land evapotranspiration (Dubbett & Werner, 2019; Good et al., 2012; Lee et al., 2007; Quade et al., 2019; Welp et al., 2008; Wen et

al., 2016) and open-water evaporation (Xiao et al., 2017), raising doubt about the reliability of the Keeling method (Lee et al., 2012; Pataki et al., 2003).

Another practical concern of the Keeling method is related to the choice of statistical method for the linear regression. Because the intercept of Eq (1) is obtained by extrapolation far beyond the observed data range, the result is very sensitive to how the regression parameters are obtained. A large body of papers have been published on this topic regarding the isotopic composition of terrestrial CO<sub>2</sub> flux (Chen et al., 2017; Kayler et al., 2010; Miller & Tans, 2003; Ogée et al., 2003; Pataki et al., 2003; Wehr & Saleska, 2017; Zobitz et al., 2006). The ordinary least squares (OLS) regression method, the most common method for estimating the regression coefficients, assumes that all measurement errors occur in the dependent variable ( $\delta$ , Eq 1) and no errors exist in the independent variable (concentration,  $c$ ). However, the concentration data can also suffer from measurement errors, especially if the measurement is made with gas flasks. For this reason, some researchers recommend that the geometric mean regression (GMR) or orthogonal distance regression (ODR) method should be used (Miller & Tans, 2003; Ogée et al., 2003; Pataki et al., 2003). Zobitz et al. (2006) applied the OLS and the GMR method to the CO<sub>2</sub>  $\delta$  and concentration time series obtained with both isotope ratio mass spectroscopy (IRMS) and isotope ratio infrared spectroscopy (IRIS) instruments, and found that the difference between the two regression methods is caused by biases in the GMR regression. Chen et al. (2017) also showed that the OLS performs better than the GMR for an IRIS instrument. More recently, Wehr and Saleska (2017) introduced a general regression method, named here the York's solution (YS) method. Because the YS method takes into account error structures of the independent and dependent variables separately and also the correlation between these two types of error, the YS

method is less biased in comparison with OLS or GMR. Wehr and Saleska (2017) argued that error correlations can arise in situations where the concentration and the  $\delta$  value are measured by the same instrument, such as an IRIS analyzer. However, information on the correlation pattern concerning IRIS instruments is lacking.

An alternative to the Keeling method is the flux-gradient (FG) method. Made possible by fast-responding IRIS instruments, the FG method determines  $\delta_E$  from the ratio of the vertical concentration gradient of the minor to that of the major isotopologue (Griffis et al. 2005; Lee et al., 2007; Wei et al., 2018; Welp et al., 2008; Wen et al., 2016; Xiao et al., 2017). The molar ratio of the  $H_2^{18}O$  flux to the  $H_2^{16}O$  flux is given by

$$R = (c_2^i - c_1^i)/(c_2 - c_1) \quad (2)$$

where  $c^i$  and  $c$  denote the hourly mean molar mixing ratio of  $H_2^{18}O$  and  $H_2^{16}O$ , respectively, and subscripts 1 and 2 denote the lower and the upper measurement level, respectively. The molar flux ratio  $R$  is then converted to the  $\delta$  scale to give  $\delta_E$ . In a typical application, an IRIS instrument samples water vapor sequentially and at a high frequency (e.g., 1 Hz) between two heights above the surface, and the gradient ratio is calculated from the high frequency data. Because a measurement period can be as short as 30 to 60 minutes in practice, this method can capture dynamic variations in  $\delta_E$ . However, the FG method becomes very noisy because of errors arising from division by small numbers. For this reason, the result is unreliable when the vertical vapor concentration difference  $c_2 - c_1$  small in magnitude, for example, under conditions of high turbulent mixing.

In this study, we evaluate a hybrid approach that combines the Keeling method with the high frequency data originally intended for FG calculation. The idea of applying the Keeling method to high frequency time series was first proposed by Bowling et al. (1999) before the emergence of the IRIS technology and was later tested with CO<sub>2</sub> isotope data collected with an IRIS instrument (Griffis et al., 2004). Because the data are collected at a high frequency, the sample size is large (typically > 700 in one hour), effectively increasing the variability in the observed water vapor concentration and decreasing the uncertainty of parameter estimation (Good et al., 2012). By restricting the regression to a short period (hourly), time variations of the source isotopic signature are not a major concern. In this paper, we are interested in whether this hybrid Keeling method can yield more robust estimates of  $\delta_E$  than the FG method under low vertical vapor gradient conditions by incorporating information on both vertical variations and temporal variations in the vapor concentration and the  $\delta^{18}\text{O}$ .

Our study builds on the work of Wehr and Saleska (2017) and Good et al. (2012). Wehr and Saleska (2017) have demonstrated the generality of the YS model for finding the best-fit straight line. Their discussion is based on synthetic datasets generated for CO<sub>2</sub> isotopes. In the present study, we extend their work to water vapor isotopes and to real data collected by two common IRIS instruments at two contrasting types of surface (a cropland and a lake). Good et al. (2012) compared uncertainties in the assessment of the isotopic composition of surface evapotranspiration among several methods (Keeling, flux-gradient and eddy covariance). Their focus is primarily on random errors of parameter estimation. Here we also examine systematic biases. The specific objectives of this study are (1) to characterize the error structures of IRIS instruments for the Keeling method involving the YS regression model, (2) to compare the

130 sysematic bias errors of the OLS, GMR and YS regression methods, and (3) to evaluate the  
131 performance of the Keeling method and the FG method under conditions of low vertical gradient  
132 of water vapor concentration.

133  
134 While random errors of the regression coefficients can be obtained with statistical  
135 methods (Good et al., 2012; Zobitz et al., 2006), assessment of bias errors requires that the true  
136 isotopic signal of the surface flux be known. In the case of a pure C<sub>3</sub> ecosystem, the <sup>13</sup>C  
137 composition of the respiration CO<sub>2</sub> flux is reasonably well constrained, and the expected <sup>13</sup>C  
138 signal (e. g., about -25‰; Wehr et al., 2016) can be used to benchmark the bias errors of  
139 regression models and regression methods (Chen et al., 2017; Zobitz et al., 2006). In other  
140 situations, the isotopic composition of the surface flux is not known *a priori*. To overcome this  
141 problem, some researchers used synthetic data that combines a hypothetical flux isotopic signal  
142 with random variations superimposed on the concentration and the  $\delta$  variable (Chen et al., 2017;  
143 Kayler et al., 2010; Vardag et al., 2016; Wehr & Saleska, 2017; Zobitz et al., 2006). In this study,  
144 we assume that the flux-gradient method provides an unbiased estimate of  $\delta_E$  under high vertical  
145 vapor gradient conditions and can be used to evaluate bias errors associated with the Keeling  
146 method. Additionally, for our lake site, the “true”  $\delta_E$  is also obtained from the Craig-Gordon  
147 model of the isotopic composition of open-water evaporation (Craig & Gordon, 1965) with a  
148 locally calibrated kinetic fractionation factor (Xiao et al., 2017).



## 2 Materials and Methods

### 2.1 Sites and instruments

The datasets used in this study were obtained in two field experiments. The first experiment was conducted in an irrigated maize field in Zhangye, Gansu Province, in Northwest China (38° 51' N, 100° 22' E) in 2012 (Wen et al., 2016). The fetch was larger than 200 m in all wind directions. Climate in Zhangye is arid with an annual mean temperature of 7.4 °C and mean annual precipitation of 129 mm. The H<sub>2</sub>O, HDO and H<sub>2</sub><sup>18</sup>O concentrations were measured at two heights (0.5 m and 1.5 m) above the canopy with an IRIS water vapor isotope analyzer (Model L1102-i, Picarro Inc. CA, USA) at 0.2 Hz. The hourly precision for the vapor  $\delta^{18}\text{O}$  is ~0.1‰ (Wen et al., 2012b). Switching between the two intake heights occurred every 2 min. The last 8 datapoints after each switching, corresponding to the last 40 seconds, were saved for the analysis. The analyzer was calibrated in-situ with a liquid vaporization module (Picarro Inc) and a CTC Analytics Prep and Load liquid autosampler (LEAP Technologies, Carrboro, NC, USA) using a single liquid water standard with a  $\delta^{18}\text{O}$  value of -14.29‰. There were 3 concentrations of calibration vapor, each measured for 25 min. After each calibration vapor, three hours were spent on the measurement of ambient air. A linear interpolation between two consecutive calibration cycles was used to obtain the span for correcting the ambient air measurement (Huang & Wen, 2014; Wen et al., 2008, 2012a).

The other experiment was conducted at Meiliangwan (MLW, 31° 15' N, 120° 13' E) in the northern part of Lake Taihu as part of the Taihu Eddy Flux Network (Lee et al., 2014) between August 2012 and September 2016. Lake Taihu is located in the Yangtze River Delta, Eastern China. The annual mean temperature is 16.2 °C and the mean annual precipitation is 1,120 mm.

The H<sub>2</sub>O, HDO and H<sub>2</sub><sup>18</sup>O concentrations were measured at two heights (1.1 m and 3.5 m) above the water surface with an IRIS water vapor isotope analyzer (Model 911-0004; Los Gatos Research, Mountain View, CA, USA) at 1 Hz. The 2-min precision of this instrument for the vapor  $\delta^{18}\text{O}$  is 0.2‰ (Xiao et al., 2017). Switching between the two intakes occurred every 30 s, with the last 15 datapoints, corresponding to the last 15 seconds, used for gradient calculations. The measurement site was located at a linear distance of 250 m from the northern shore. To minimize land influence on the measurement, we restricted our analysis to the data collated in the wind direction sector of 140° to 315°, corresponding to a fetch of 8 to 50 km. The in-situ calibration vapor was generated by a water vapor isotope standard source (Model 908-0003-9002; Los Gatos Research). The calibration was performed every 3 h. Each calibration cycle consisted of 5 concentrations and lasted for 30 min in total. Other details of this experiment can be found in Xiao et al. (2017).

## 2.2 Regression methods

In this study, three regression methods were used in the Keeling method to obtain the intercept of a linear equation  $y = a + bx$ : ordinary least squares regression (OLS), geometric mean regression (GMR), and York's solution (YS). The OLS seeks to minimize the sum of the squared residuals between the expected values of the dependent variable  $y$  and the data points. The result is unbiased only if errors in the independent variable  $x$  are negligible and errors in the dependent variable  $y$  are constant. The slope  $b$  and intercept  $a$  can be expressed as,

$$b_{\text{OLS}} = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sum(x_i - \bar{x})^2} \quad (3)$$

$$a_{\text{OLS}} = \bar{y} - b_{\text{OLS}}\bar{x} \quad (4)$$

where  $x_i$  and  $y_i$  are observed values, and  $\bar{x}$  and  $\bar{y}$  are the corresponding mean values. The standard error of slope  $b$  obtained with OLS,  $\sigma_b$ , can be expressed as

$$\sigma_{bOLS} = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{(n-2) \sum (x_i - \bar{x})^2}} \quad (5)$$

and the standard error of intercept obtained with OLS,  $\sigma_a$ , can be expressed as

$$\sigma_{aOLS} = \sqrt{\frac{\sigma_b^2 \sum x_i^2}{n}} \quad (6)$$

where  $n$  is the number of datapoints and  $\hat{y}_i$  is the expectation values of  $y_i$ ,  $\hat{y}_i = b_{OLS}x_i + a_{OLS}$ .

The GMR seeks to minimize both the vertical (dependent variable,  $y$ ) and horizontal (independent,  $x$ ) residuals. The result is unbiased only when the error in  $x$  divided by the variance of  $x$  is equal to the error in  $y$  divided by the variation of  $y$  (Kermack & Haldane, 1950). The slope  $b$  and intercept  $a$  can be expressed as,

$$b_{GMR} = \sqrt{b_{yx} \frac{1}{b_{xy}}} \quad (7)$$

$$a_{GMR} = \bar{y} - b_{GMR}\bar{x} \quad (8)$$

where both  $b_{yx}$  and  $b_{xy}$  are obtained from the OLS, but they have different independents:  $b_{yx}$  is the slope when  $x$  is chosen as the independent variable, and  $b_{xy}$  is the slope when  $y$  is chosen as the independent variable. Eqs (5) and (6) can also be used to obtain  $\sigma_b$  and  $\sigma_a$  of the GMR, where the expected  $y_i$  is obtained with the GMR regression coefficients (Eqs 7 and 8).

There is a relationship between the slope obtained with GMR and OLS,

$$b_{GMR} = \frac{b_{OLS}}{|r|} \quad (9)$$

where  $r$  is Pearson's correlation coefficient between  $x$  and  $y$ .

Generally, both  $x$  and  $y$  have measurement errors, and these errors may also be correlated. While neither the OLS nor the GMR method accounts for the error correlation, the YS method takes the correlation between errors in  $x$  and errors in  $y$  into account to obtain a best-fit straight line (York, 1966, 1969; York et al., 2004). The slope and intercept from YS can be expressed as,

$$b_{YS} = \frac{\sum W_i \beta_i (x_i - \bar{x})}{\sum W_i \beta_i (y_i - \bar{y})} \quad (10)$$

$$a_{YS} = \bar{y} - b_{YS} \bar{x} \quad (11)$$

where  $\bar{x}$  and  $\bar{y}$  are weighted means of  $x$  and  $y$

$$\bar{x} = \frac{\sum W_i x_i}{\sum W_i}, \bar{y} = \frac{\sum W_i y_i}{\sum W_i} \quad (12)$$

and  $\beta_i$ , an intermediate variable, is given by

$$\beta_i = W_i \left[ \frac{x_i - \bar{x}}{\omega(y_i)} + \frac{b(y_i - \bar{y})}{\omega(x_i)} - (b(x_i - \bar{x}) + (y_i - \bar{y})) \frac{r_i}{\sqrt{\omega(x_i)\omega(y_i)}} \right] \quad (13)$$

In Eq (13),  $b$  is an initial guess of the slope which can be obtained from the OLS regression,  $r_i$  is correlation between errors in  $x_i$  and errors in  $y_i$ , and  $\omega(x_i)$  and  $\omega(y_i)$  are weights of  $x_i$  and  $y_i$  given by

$$\omega(x_i) = \frac{1}{\sigma^2(x_i)}, \omega(y_i) = \frac{1}{\sigma^2(y_i)} \quad (14)$$

where  $\sigma(x_i)$  and  $\sigma(y_i)$  are errors in horizontal ( $1/c$ ) and vertical ( $\delta^{18}\text{O}$ ) coordinates at the  $i$ th data point. The intermediate variable  $W_i$  in Eqs (11) and (12), or the weight of  $i$ th point, is given by

$$W_i = \frac{\omega(x_i)\omega(y_i)}{\omega(x_i) + b^2\omega(y_i) - 2br_i\sqrt{\omega(x_i)\omega(y_i)}} \quad (15)$$

Typically, the number of iterations is less than 10 from the initial to the final slope value. The standard error of slope obtained with YS can be expressed as

$$\sigma_{bYS} = \sqrt{\frac{1}{\sum W_i (x_i - \bar{x})^2}} \quad (16)$$

and the standard error of intercept obtained with YS can be expressed as

$$\sigma_{aYS} = \sqrt{\sigma_b^2 \bar{X}^2 + \frac{1}{\sum w_i}} \quad (17)$$

where  $X_i = \bar{x} + \beta_i$  and  $\bar{X} = \frac{\sum w_i X_i}{\sum w_i}$ .

### 2.3 Characterization of error structures

The error parameters in the YS method,  $\sigma(x_i)$ ,  $\sigma(y_i)$  and  $r_i$ , for Lake Taihu were determined with the field calibration data. A calibration cycle consisted of 5 concentrations, each lasting for 6 min. An example of the calibration stepping is given by Xiao et al. (2017; their Figure 4). The standard deviation of  $1/c$ , the standard deviation of  $\delta^{18}\text{O}$  and the correlation coefficient between  $1/c$  and  $\delta^{18}\text{O}$  were calculated for each concentration interval. We assume that these variations originated purely from measurement errors. The data during transition from one concentration level to the next were excluded from the calculation.

For Zhangye, the field calibration data cannot be used to characterize the measurement errors because the concentration of the water vapor generated by the liquid vaporization module was not stable during the calibration phase. To obtain the error parameters, we carried out additional measurements in the laboratory using the same IRIS water vapor isotope analyzer deployed in the field. The analyzer was configured to measure the water vapor concentration and the isotopic composition of a water vapor stream generated by a standard delivery module (Model A0101; Picarro Inc.). The delivery module was fed with liquid water of known  $\delta^{18}\text{O}$  value (-9.17‰). Each measurement cycle included 3 water vapor concentrations and lasted for 1 h. A total of 141 measurement cycles were performed, with the vapor concentration ranging from

7,900 ppm to 27,690 ppm. The same method used for Lake Taihu was deployed to obtain the error parameters.

## 2.4 Data processing

The high-frequency IRIS data were used to calculate  $\delta_E$  for each hourly observation interval using the three regression methods described above. Each observation, including data obtained for both measurement heights, consisted of about 200 and 1,800 data points for Zhangye and Lake Taihu, respectively. Figure 1 shows the time series of the water vapor mixing ratio and the calibrated vapor  $\delta^{18}\text{O}$  from a typical observation period at Lake Taihu, and Figure 2 shows the corresponding linear regression plot. The  $\delta_E$  estimated from the Keeling method was then compared with the  $\delta_E$  obtained from the FG method. Additionally, at Lake Taihu, comparison was also made with the Craig-Gordon model calculation of the lake evaporation delta using a locally-tuned kinetic fractionation factor (Xiao et al., 2017).

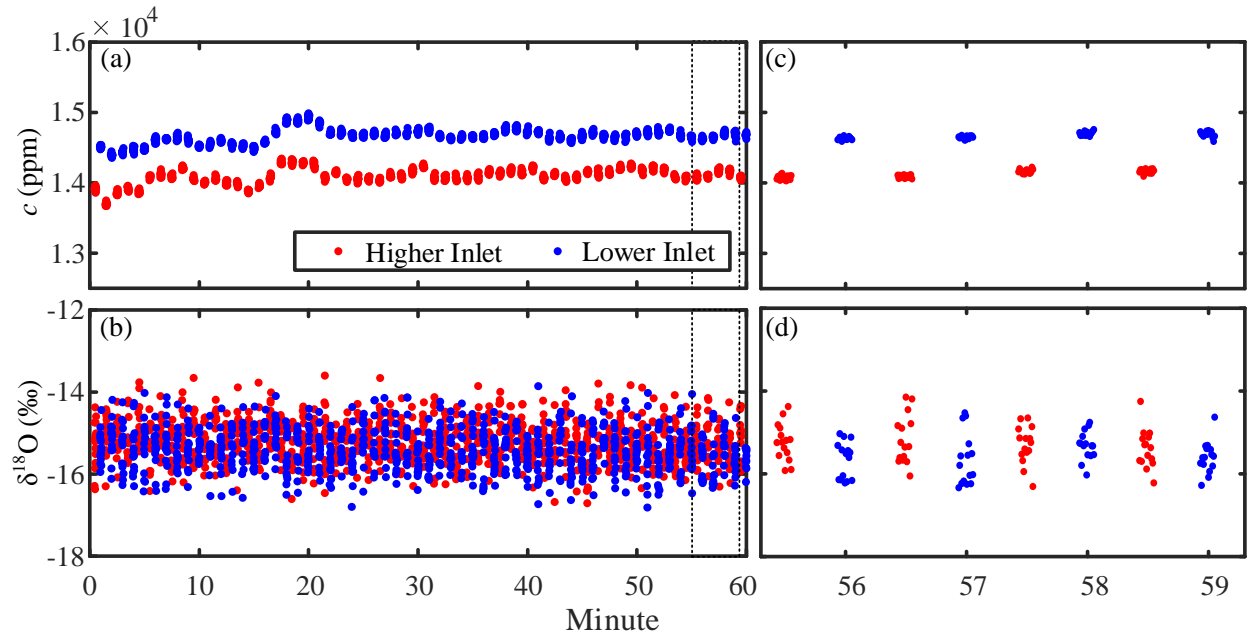


Figure 1. Temporal variation of  $\text{H}_2\text{O}$  mixing ratio (a) and  $\delta^{18}\text{O}$  (b) at the lower inlet (blue dots) and higher inlet (red dots) at Lake Taihu between 16:00 and 17:00 local time on October. 22<sup>nd</sup>, 2014. Panels c and d are the corresponding zoom-in plot of the dotted box in panels a and b.

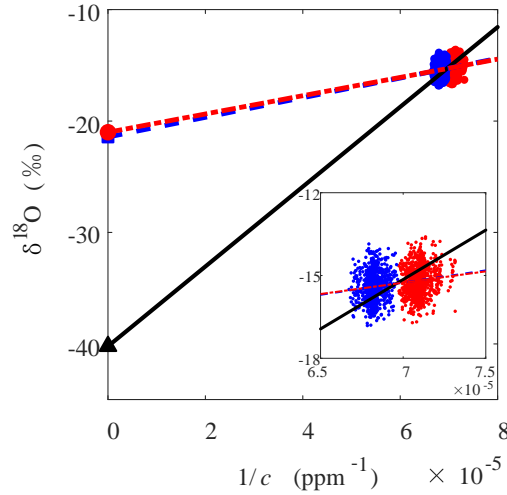


Figure 2. An illustration of the three regression methods applied to the data in Figure 1. YS: red-dot-dashed line; OLS: blue-dashed line; GMR: black-solid line; blue dots: observations at lower inlets; red dots: observations at higher inlet. In this hour, the  $\delta_E$  obtained from the FG method is -21.0‰, with a standard deviation 4.78‰.

Three criteria were used to screen the data. The FG method becomes noisy at times of small vertical concentration gradients. To ensure a robust comparison, we restricted most of our analysis to observations whose hourly mean vertical vapor concentration difference between the two measurement heights is larger than 200 ppm in magnitude. About 2/3 of the 3,026 and 1,622 valid observations satisfy this criterion at Zhangye and Lake Taihu, respectively. The second criterion was the standard deviation of  $\delta_E$  calculated by the FG method; we used a threshold value of 20‰. The third criterion required that the  $P$  value obtained from the Keeling method be smaller than 0.05 to ensure that the relationship between  $1/c$  and  $\delta^{18}\text{O}$  passes the significance test

(Unger et al., 2010). A total of 1,084 and 817 hourly observations remained for Zhangye and Lake Taihu, respectively, after the data screening.

### 3 Results and Discussion

#### 3.1 Error structures of the vapor concentration and the isotope composition

The relationships between the water vapor concentration and the standard deviation of  $1/c$ , the standard deviation of  $\delta^{18}\text{O}$  and correlation coefficient  $r$ , established with the data collected during the instrument calibration cycles, are shown in Figure 3. Unsurprisingly, the standard deviation of  $1/c$  was greater at lower concentrations, with the Picarro analyzer (used at Zhangye) and the LGR analyzer (used at Lake Taihu) giving similar performance. The standard deviation of  $1/c$  was  $4.02 \times 10^{-7}$  and  $3.37 \times 10^{-7} \text{ ppm}^{-1}$  at a water vapor concentration of 10,000 ppm and  $1.29 \times 10^{-7}$  and  $9.40 \times 10^{-8} \text{ ppm}^{-1}$  at a concentration of about 30,000 ppm, for Zhangye and Lake Taihu, respectively. The standard deviation of  $\delta^{18}\text{O}$  showed opposite trends for the two sites. At Zhangye, the standard deviation of  $\delta^{18}\text{O}$  was relatively constant at concentrations lower than about 20,000 ppm and increased with increasing concentration beyond this threshold. At Lake Taihu, the standard deviation of  $\delta^{18}\text{O}$  showed a general decreasing trend with increasing concentration. At Zhangye, the correlation between measurement errors in  $1/c$  and in  $\delta^{18}\text{O}$  was slightly positive at low concentrations ( $\sim 10,000$  ppm) and varied around zero at high concentrations ( $\sim 25,000$  ppm). At Lake Taihu, the error correlation was mostly positive and did not seem to depend on the vapor concentration.



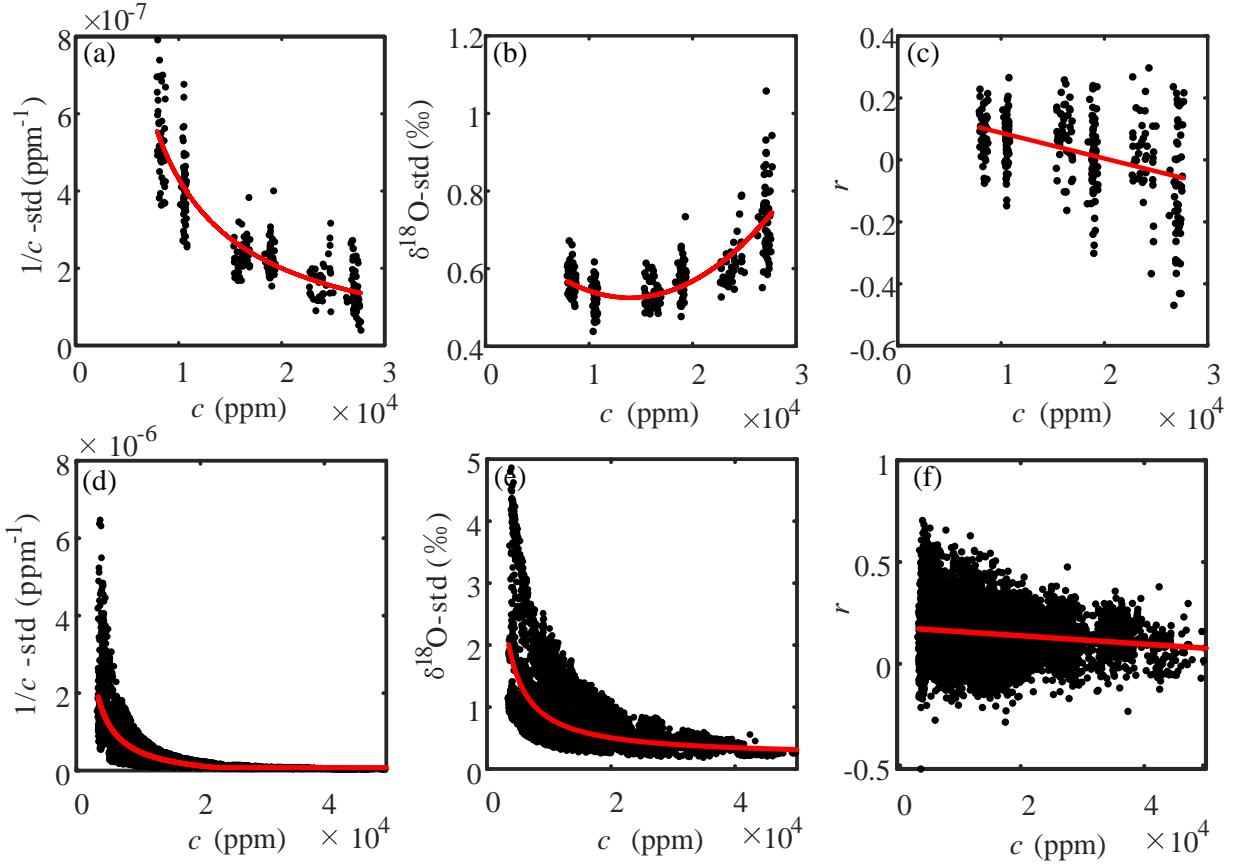


Figure 3. Relationships between water vapor concentration and errors in  $1/c$ , errors in  $\delta^{18}\text{O}$  and correlation coefficient between errors in  $\delta^{18}\text{O}$  and errors in  $1/c$  for Zhangye (a, b and c) and Lake Taihu (d, e and f). The solid red line in each panel indicates the regression fit, with the regression equation given in Supplementary Table S1.

Results of regression fitting to the data shown in Figure 3 are summarized in Supplementary Table S1. These regression equations were used to determine parameters  $\sigma(x_i)$ ,  $\sigma(y_i)$  and  $r_i$  in Eqs (14) and (15) as functions of  $c_i$ . For example, the error in the vertical axis ( $\delta^{18}\text{O}$ ) at time  $i$  is given as  $\sigma(y_i) = f_y(c_i)$ , where  $f_y$  is the regression fitting equation, and  $c_i$  is the measured concentration at time  $i$ . Our method for determining these error parameters differs from that used by Wher and Saleska (2017). In their study, errors in the horizontal and the

vertical axis are set to prescribed hourly instrument precisions and the correlation between these two errors is set to zero. Compared with the precision of the instrument, the parameters  $\sigma(x_i)$  and  $\sigma(y_i)$  in this study were larger because of random errors at high sampling frequencies and were more realistic representations of the actual measurement errors in field conditions.

### 3.2 Comparison of regression methods

Figure 4 compares  $\delta_E$  determined with the FG method and the Keeling intercept using the three regression methods. Each data point represents one hourly  $\delta_E$  calculated using data from two measurement heights above the surface. The  $\delta_E$  values based on the YS and OLS regression method were comparable with the FG results. The two methods yielded similar mean bias errors (YS: 1.08‰; OLS: 0.92‰) at Zhangye, and OLS slightly outperforms YS at Lake Taihu, with a mean bias 1.05‰ for YS and 0.14‰ for OLS. In contrast, the GMR results were rather poor, with large mean bias errors (6.97 and -1.66‰ for Zhangye and Lake Taihu, respectively) and large scatters (low linear correlation  $R$  values).

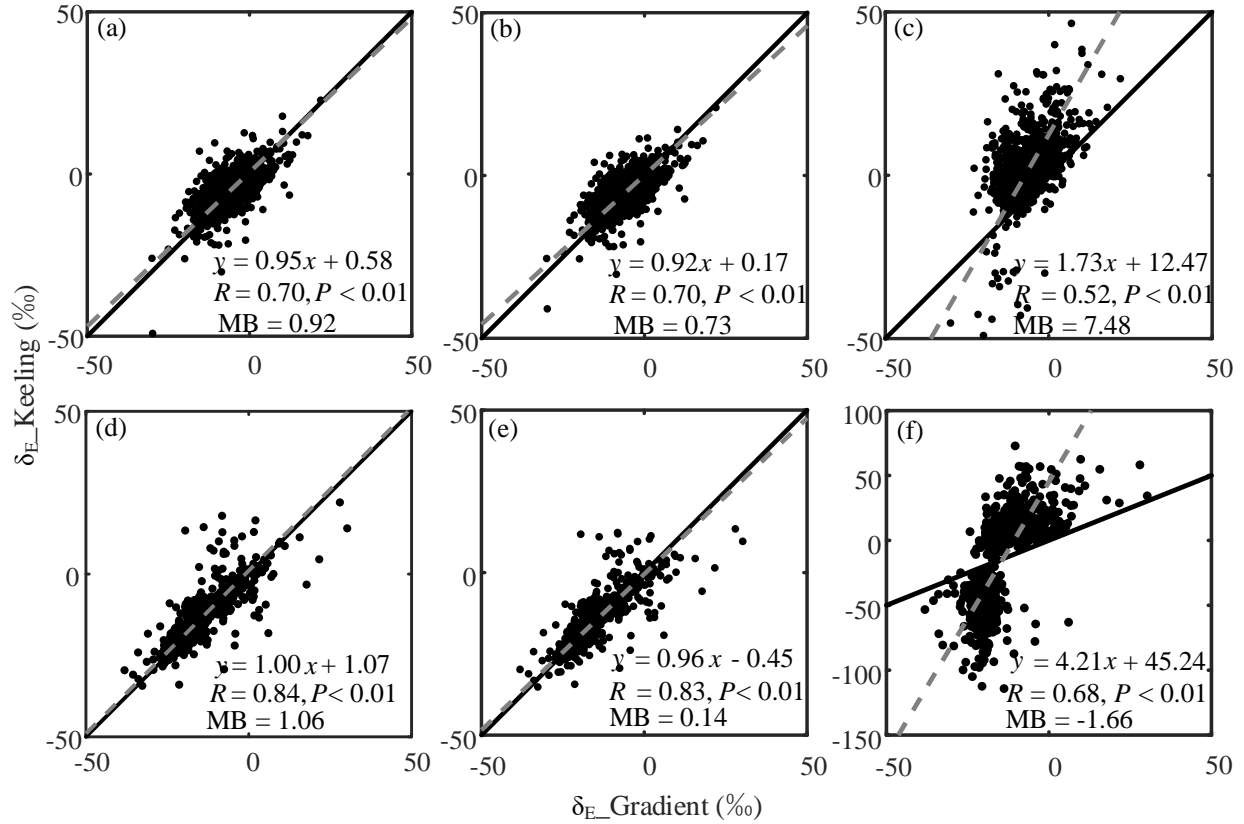


Figure 4. Comparison of the evaporation isotopic signature  $\delta_E$  obtained with the flux-gradient method and with the Keeling method for Zhangye (a, b and c) and Lake Taihu (d, e and f). Panels a and d: YS regression; panels b and e: OLS regression; panels c and f: GMR regression. Solid black lines are the 1:1 comparison and the regression equation is listed for each panel along with the correlation coefficient,  $R$ , significance,  $P$ , and mean bias (MB, ‰).

An implicit assumption of GMR is that the normalized errors in  $x$  and  $y$  are equal (Kermack & Haldane, 1950). This assumption is not satisfied here. Table 1 shows the mean errors in  $1/c$  and  $\delta^{18}\text{O}$ , and these errors normalized by the ranges of  $1/c$  and  $\delta^{18}\text{O}$  for three levels of water vapor concentration. Here the range of a variable is defined as the difference between the maximum and the minimum value of the high-frequency data in a given 60-min observational period. Errors existed both in the horizontal coordinate  $1/c$  and the vertical

349 coordinate  $\delta^{18}\text{O}$ . The normalized error in  $\delta^{18}\text{O}$  was, however, much larger than the normalized  
350 error in  $1/c$ , by a factor of 6 to 10 at Zhangye and of 3 to 7 at Lake Taihu.

Table 1. Measurement errors in three quantiles of water vapor concentration. Errors are calculated as one standard deviation of high frequency data (0.2 Hz at Zhangye and 1 Hz at Lake Taihu). Here  $c$  and  $\delta^{18}\text{O}$  denotes water vapor concentration and vapor  $^{18}\text{O}$  isotope ratio, respectively.

Quantile	Mean $c$ ppm	Error in $1/c$ $\text{ppm}^{-1}$	Error in $\delta^{18}\text{O}$ ‰	$c$ range ppm	$\delta^{18}\text{O}$ range ‰	$1/c$ range $\text{ppm}^{-1}$	Error in $1/c$ / ( $1/c$ range)	Error in $\delta^{18}\text{O}$ / ( $\delta^{18}\text{O}$ range)
Zhangye								
0 - 25	7688	$5.86 \times 10^{-7}$	0.57	1856	3.48	$3.64 \times 10^{-5}$	0.016	0.16
25 - 75	12984	$3.32 \times 10^{-7}$	0.53	2659	3.50	$1.65 \times 10^{-5}$	0.020	0.15
75 - 100	18930	$2.16 \times 10^{-7}$	0.55	3566	3.95	$1.02 \times 10^{-5}$	0.021	0.14
Lake Taihu								
0 - 25	9171	$5.73 \times 10^{-7}$	0.88	1262	7.43	$1.73 \times 10^{-5}$	0.033	0.12
25 - 75	21213	$1.02 \times 10^{-7}$	0.49	1697	3.29	$4.27 \times 10^{-6}$	0.024	0.15
75 - 100	30879	$7.87 \times 10^{-8}$	0.40	2232	3.11	$2.35 \times 10^{-6}$	0.033	0.13

Strictly, the OLS regression is unbiased only if no errors exist in  $1/c$ . But because the normalized error in  $1/c$  was several times smaller than the normalized error in  $\delta^{18}\text{O}$ , the OLS regression yielded robust results. Similar conclusions have been reported by Zobitz et al. (2006), Chen et al. (2017) and Wehr and Saleska (2017) for carbon isotopes of  $\text{CO}_2$ . In their studies, the relative error in  $\delta^{13}\text{C}$  measurements is larger than relative error in  $\text{CO}_2$  concentration measurements, so the OLS provides better results than the GMR. Wehr and Saleska (2017) cautioned that OLS will introduce obvious bias if the relative error in  $\text{CO}_2$  concentration measurements is large or the relative error in  $\delta^{13}\text{C}$  measurements is small.

Zobitz et al. (2006) concluded that the bias error associated with the GMR is mathematical in nature. Pataki et al. (2003) reported that the GMR intercept is systematically more negative than the OLS intercept when applied to the calculation of the  $^{13}\text{C}$  composition of ecosystem respiration. In our study, the  $\delta_E$  from the GMR could be biased either high or low. At Zhangye, almost all the datapoints were located above the 1:1 line (Figure 4c), indicating a high bias, while at Lake Taihu, the bias was mostly positive when the  $\delta_E$  from the Keeling method with the GMR was greater than  $-15\text{‰}$  and mostly negative when  $\delta_E$  was less than  $-15\text{‰}$ .

### **3.3 Dependence on water vapor concentration range**

It is well established that increasing the  $\text{CO}_2$  concentration range will reduce the standard error as well as the systematic bias associated with the  $^{13}\text{C}$  signature of the respiration  $\text{CO}_2$  flux inferred from the Keeling method. This is true for observations made with flasks (Pataki et al., 2003; Zobitz et al., 2006) and IRIS instruments (Chen et al., 2017; Zobitz et al., 2006) and for synthetic  $\text{CO}_2$  datasets (Kaylor et al., 2010; Wehr & Saleska, 2017). Whether these findings can

be extended to water vapor observations is not known. Here this range effect is examined from three perspectives. First, we find that the standard error of the  $\delta_E$  estimate showed strong dependence on the water vapor concentration range, the maximum minus the minimum water vapor concentration during each hourly observation (Figure 5 and Supplement Table S2). At both sites, the uncertainty of  $\delta_E$  decreased with increasing concentration range. Although all the three regression methods yielded a linear relationship on the log-log scale, the range dependence of the YS method (Figure 5a and 5d) was much tighter than those of the OLS (Figure 5b and 5e) and the GMR method (Figure 5c and 5f). So from the standpoint of predicting the uncertainty of individual observations, YS was better than the other two regression methods. The log-log relationship was also reported by Good et al. (2012) for water vapor. Chen et al. (2017) compared the OLS and the GMR methods using data obtained with an IRIS CO<sub>2</sub> analyzer and found that the OLS method produces smaller standard errors than the GMR method.

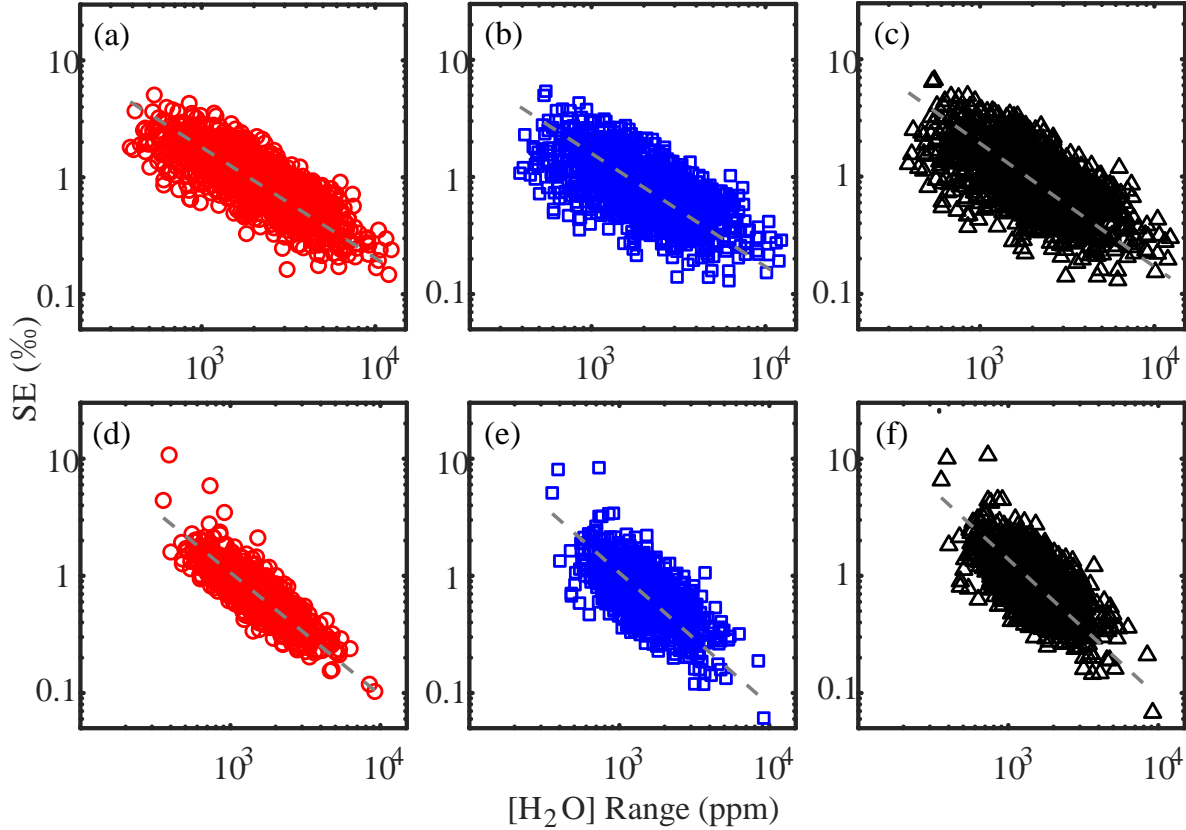


Figure 5. Relationships between the water vapor concentration range and the standard error of the Keeling method with the YS (a and d), the OLS (b and e) and the GMR regression (c and f) based on the two-height data at Zhangye (a, b and c) and Lake Taihu (d, e and f). Also shown are the best fit lines, with the regression statistics given in Supplementry Table S2.

Second, the bias errors associated with the YS and OLS regression did not show obvious dependence on concentration range (Figure 6). In other words, a larger concentration range helped to reduce random errors of the parameter estimate of these two methods but did not bring obvious improvement to their systematic bias errors. For comparison, the GMR estimate of  $\delta_E$  was biased high at Zhangye, in reference to the  $\delta_E$  obtained with the FG method, and the systematic bias increased with decreasing concentration range (Figure 6a). At Lake Taihu, the



GMR result was biased high at high concentration ranges and biased low at low ranges (Figure 6b).

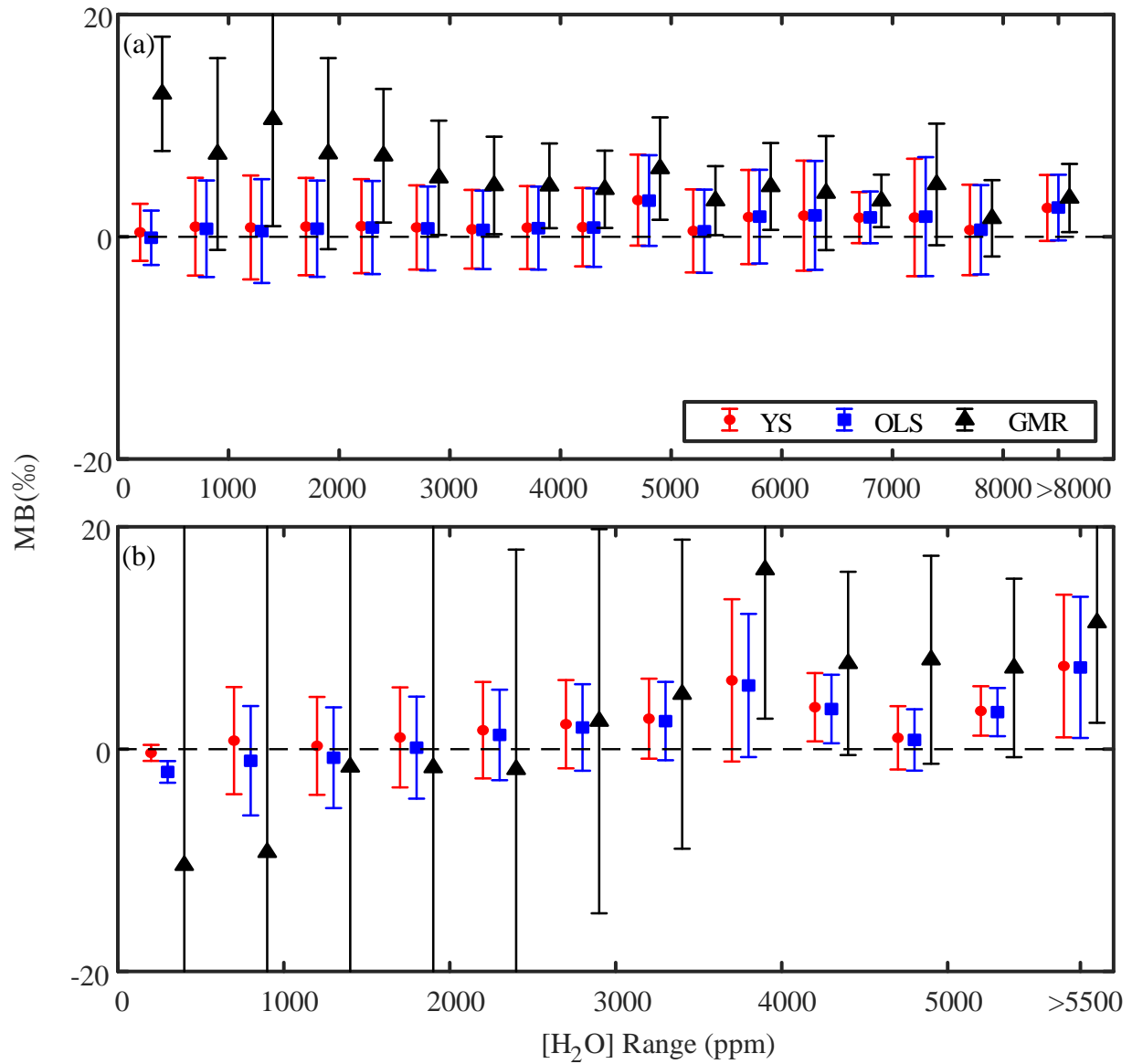
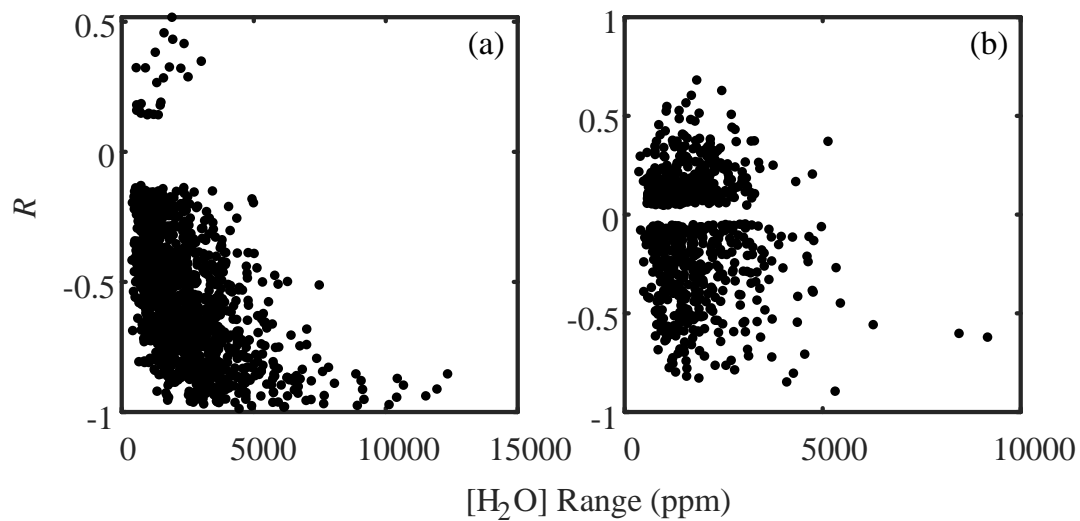


Figure 6. Mean bias of the evaporation isotope ratio (Keeling estimate minus the FG value) as a function of the water vapor concentration range at Zhangye (a) and Lake Taihu (b). Error bars are standard deviation of the bias for each bin.

Third, the correlation between  $1/c$  and  $\delta^{18}\text{O}$  generally improved with increasing concentration range (Figure 7). This correlation pattern explains in part why the systematic bias error of the GMR intercept was larger at lower concentration ranges (Figure 6). Figure 8 shows that the systematic bias error of the GMR method was sensitive to the sign of the correlation, showing positive biases at times of negative correlation and vice versa. At the Zhangye cropland, the correlation between  $\delta^{18}\text{O}$  and the inverse of the vapor concentration was negative for 98% of the observations (Figure 8a), and the GMR bias error was mostly positive (Figures 4c and 6a). At Lake Taihu, the correlation was negative for 53% and positive for 47% of the observations (Figure 8b), explaining the bifurcation pattern shown in the 1:1 plot (Figure 4f). According to Eq (9), the slope  $b_{\text{GMR}}$  of the GMR regression is larger in magnitude than the slope  $b_{\text{OLS}}$  of the OLS regression. In cases of positive  $R$ , the regression slope is positive and a larger positive slope leads to a negative bias of the GMR intercept. Conversely, in cases of negative  $R$ , a more negative slope leads to a positive bias of the intercept.

In the  $\text{CO}_2$  isotopic studies, increasing the absolute correlation coefficient is also an effective way to decrease the bias of the result obtained by the GMR method (Bowling et al., 2005; Chen et al., 2017; Zobitz et al., 2006). In these studies, the correlation between  $\delta^{13}\text{C}$  and the inverse of the  $\text{CO}_2$  concentration is generally positive, so the bias in the GMR intercept is generally negative (Pataki et al., 2003).



429

430 Figure 7. Relationship between the Pearson's correlation coefficient (between the inverse of the  
 431 vapor concentration and the vapor  $\delta$  value) and  $\text{H}_2\text{O}$  range at Zhangye (a) and Lake Taihu (b).

432 Each datapoint represents one hourly observation including data from two measurement heights.

433 All the observations shown here passed the significance test ( $P < 0.05$ ).

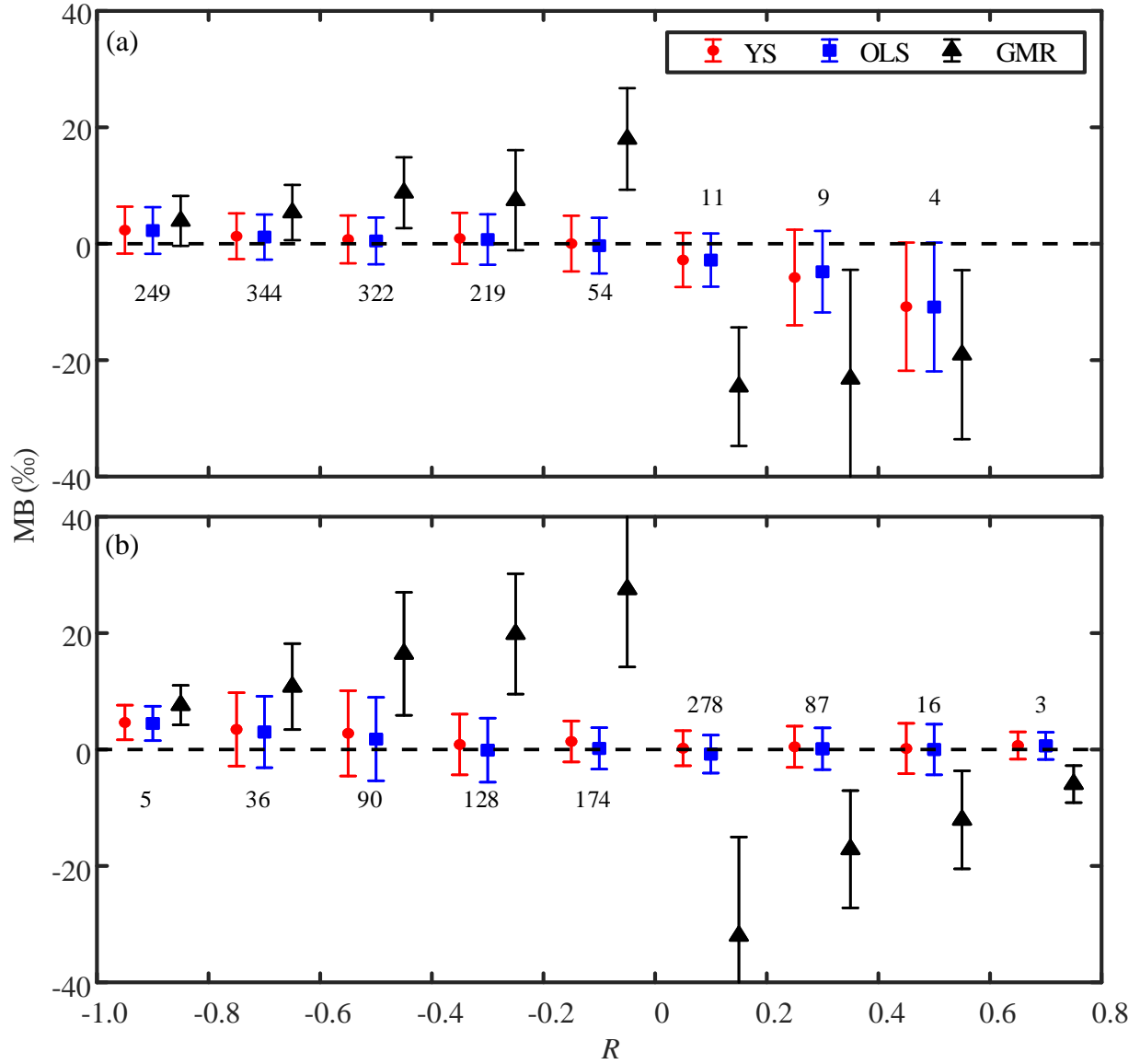


Figure 8. Mean bias of the evaporation isotope ratio  $\delta_E$  (Keeling estimate minus FG value) as a function of the correlation coefficient  $R$  between the inverse of the concentration and the vapor  $\delta$  value at Zhangye (a) and Lake Taihu (b). All the observations used here for bin averaging passed the 0.05 significance test. Also shown is the number of observations for each bin.

At Lake Taihu, the bias errors of the OLS and YS methods were not sensitive to the correlation strength. At Zhangye, their errors were not sensitive to the correlation strength if the

correlation is negative. If the correlation is positive, the OLS and YS showed similar high biases of -4.90‰ to -5.25‰ (bin averages), but that may be because the number of samples used for bin averaging was very small ( $< 12$  datapoints per bin) for Zhangye.

### **3.4 Results from single-height data**

In this section, we evaluate the three regression models using high frequency data collected at a single height. Logistically, it is much easier to measure the water vapor isotopic composition at a single height than at multiple heights involving valve switching. Indeed, the great majority of the published IRIS water vapor isotope measurements was conducted with a single-height configuration (Fiorella et al., 2018; Wei et al., 2019; Yao et al., 2018; Zannoni et al., 2019a). Figure 9 is based on the high-frequency data collected at the lower measurement height. All the three regression models performed less well when only data from the lower height were used than when data from both heights were used to determine the regression (Figure 4). For example, at Lake Taihu, the mean bias error of the OLS changed to -2.82‰ (Figure 9e) from 0.14‰ (Figure 4e) and the correlation between the Keeling and the FG method was reduced to 0.26 from 0.83. Use of the data collected at the upper height yielded essentially the same conclusion (Supplementary Figure S1).

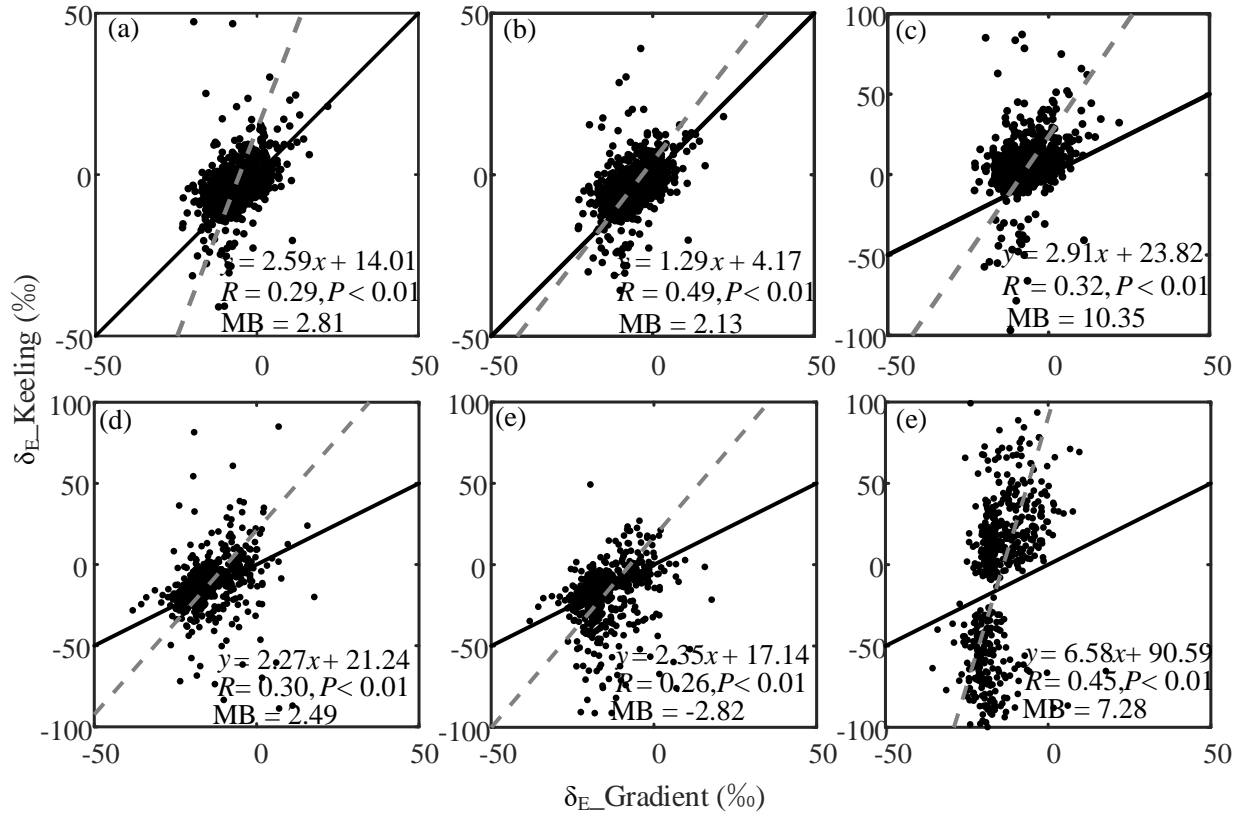


Figure 9. Same as Figure 4 except that only the data observed at the lower measurement inlet was used for the Keeling analysis.

The deteriorated performance in Figure 9 resulted in part from a reduced sample size and from a narrower concentration range. The sample size was halved when only one-height measurement was used. In the example shown in Figure 1, the concentration range is 673 and 1,318 ppm for the data at the lower height and for both heights, respectively. The mean concentration ranges were 2,063 and 1,137 ppm for Zhangye and Lake Taihu, respectively, for the data shown in Figure 9, whereas the mean ranges were larger, at 2,534 and 1,712 ppm for Zhangye and Lake Taihu, respectively, in Figure 4. The standard error of the intercept was larger with one-height measurements than with two-height measurements (Supplementary Figure S2). Similarly, Good et al. (2012) reported that the uncertainty of the isotopic composition of

evapotranspiration associated with high-frequency time series measured at a single height is 25% larger than with a combined use of time series measured at multiple heights.

While the systematic biases of the GMR regression in Figure 9 (panels c and f) are mathematical in nature (as in Figure 4 panels c and f), the biases of the OLS and the YS regression here may be related to footprint influences, especially at Zhangye where the fetch was short (about 200 m). At Zhangye, 70% and 68% of the data points lay above the 1:1 line (Figure 9 panels a and b), and the mean biases were 2.81‰ and 2.13‰, for YS and OLS, respectively. Griffis et al. (2007) found that the Keeling plot method with one-height data yields lower estimates of the  $^{13}\text{C}$  composition of ecosystem respiration of a  $\text{C}_4$  crop than the FG method. They attributed this difference to a footprint mismatch: the single-height concentration has a much larger source area and is therefore more influenced by the surrounding  $\text{C}_3$  crops, than the FG data. Interestingly, Good et al. (2012) also found higher  $\delta_{\text{E}}$  values with the Keeling method using single-height data than using data from multiple heights (mean difference about 16‰ for  $^{18}\text{O}$ , black triangles in their Figure 8).

### 3.5 Performances under low vertical vapor gradient conditions

To determine whether the Keeling method gives a more robust estimate of  $\delta_{\text{E}}$  than the FG method under low gradient conditions, we used the Craig-Gordon model as a reference to evaluate their performance for Lake Taihu (Figure 10). Low gradient conditions tended to occur at times of low evaporation flux at Lake Taihu and could occur at times of both low and high evaporation flux at Zhangye (Supplementary Figure S3). The results in Figure 10 are for the OLS regression. At high concentration gradients ( $> 200$  ppm), the two methods gave similar linear

correlation coefficients with the Craig-Gordon model  $\delta_E$  values (0.72 for FG and 0.66 for Keeling method with OLS), and the Keeling method with OLS had a higher RMSE (6.56‰) and a higher mean bias (0.81‰) than the FG method (6.03‰ RMSE, 0.65‰ MB). When the vapor gradient was smaller than 200 ppm in magnitude, both methods produced weaker correlation with the Craig-Gordon model results than when the gradient was larger, but the Keeling method with OLS slightly outperformed the FG method in terms of the RMSE (6.26‰ for Keeling and 7.68‰ for FG) and the mean bias (0.57‰ for Keeling and 2.61‰ for FG). If the YS regression was used, the Keeling mean bias and RMSE changed slightly to 1.76‰ and 6.83‰ at high concentration gradients and 3.03‰ and 6.95‰ at low concentration gradients, respectively (Figure S4).



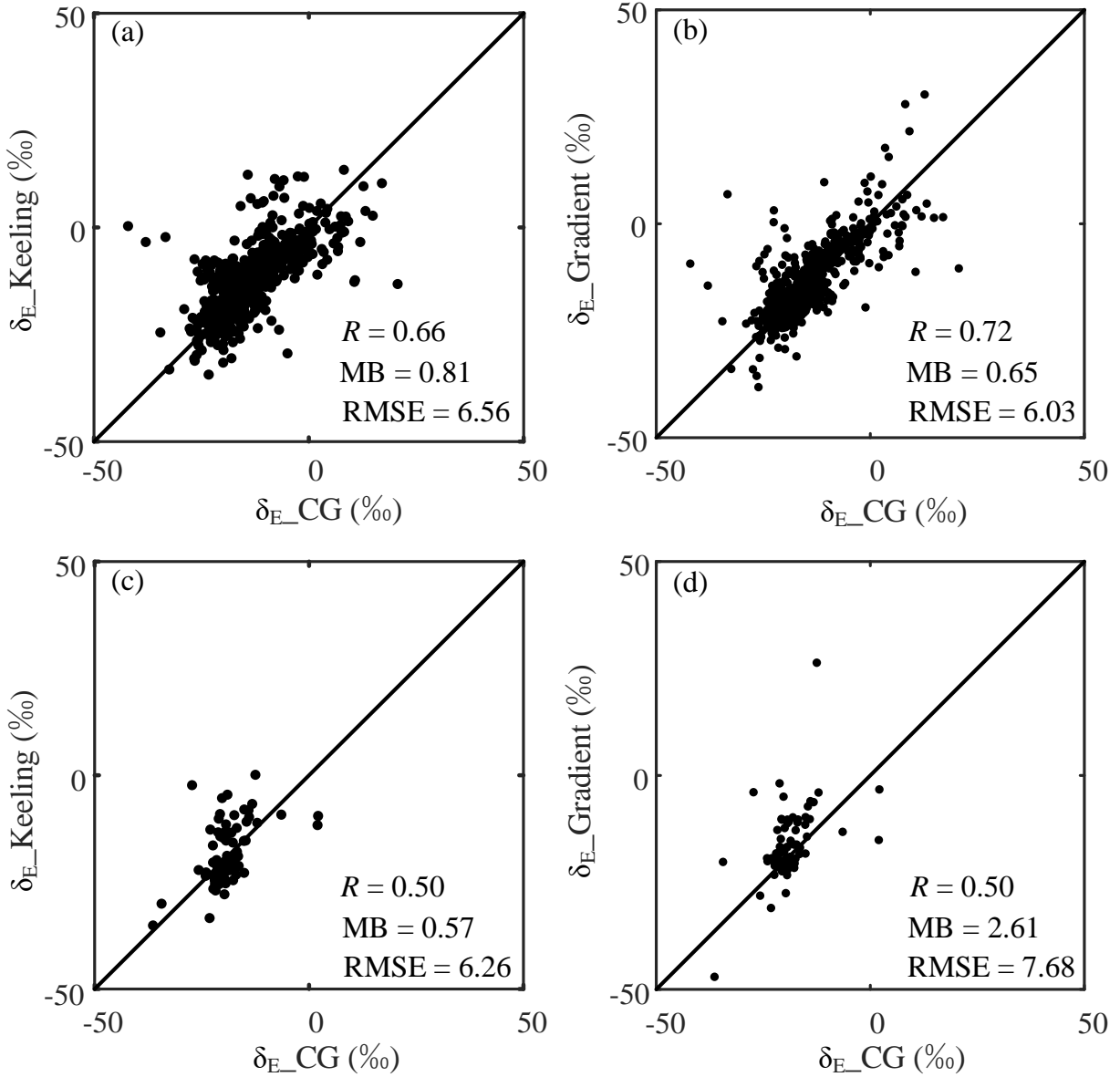


Figure 10. Comparison between the evaporation isotopic signature  $\delta_E$  calculated by the Craig-Gordon (CG) model with that from the Keeling method with the OLS regression and from the FG method at Lake Taihu. Panels a and b: observations with hourly mean vertical concentration difference greater than 200 ppm in magnitude; panels c and d: observations with hourly concentration difference smaller than 200 ppm in magnitude.

The Keeling and the FG methods are mathematically equivalent and give identical  $\delta_E$  if the same hourly concentration and hourly water vapor  $\delta$  at the two measurement heights are used to determine  $\delta_E$  (Good et al., 2012). In the present case, because the Keeling method used high-frequency data collected at both heights, it was constrained by both temporal and vertical variations. However, the FG was constrained only by vertical variations because it used the hourly means. The results given in Figure 10 suggests that the Keeling method using high frequency data may be more reliable at times of low vertical concentration gradient than the FG method because it retains temporal variability.

The measurement systems at Zhangye and Lake Taihu both deployed buffer volumes to help improve the hourly mean gradient measurements. These buffers had a time constant of about 1 min, effectively damping out turbulent fluctuations at frequencies higher than about 0.02 Hz. Measurements taken at a frequency equivalent to the inverse of the instrument response time and without physical or digital averaging (Griffis et al., 2007; Good et al., 2012) may further improve the Keeling method under low vertical gradient conditions.

#### **4 Summary and Conclusions**

The error structures of the two IRIS analyzers (a Picarro and an LGR) were characterized as functions of water vapor concentration. Both instruments showed smaller measurement errors in more humid conditions. For the Picarro analyzer used at Zhangye, the correlation between measurement errors in the inverse of the concentration and the water vapor  $\delta$  was slightly positive (about 0.09) at low concentrations ( $\sim 10,000$  ppm) and varied around zero at high

concentrations (~25,000 ppm). For the LGR analyzer used at Lake Taihu, the error correlation was mostly positive (about 0.14) and did not seem to depend on the vapor concentration.

The YS and the OLS regression method produced equally robust estimates of  $\delta_E$  for the Zhangye cropland and for Lake Taihu, with the former giving a tighter standard error structure than the latter. The mean bias error was 0.92‰ and 1.06‰ for YS and 0.73‰ and 0.14‰ for OLS, at Zhangye and Lake Taihu, respectively. The GMR method was systematically biased high (8.10‰ and 21.44‰ at Zhangye and Lake Taihu, respectively) when the linear correlation  $R$  between the inverse of the vapor concentration and the vapor  $\delta$  value was negative and biased low (-23.12‰ and -27.60‰ at Zhangye and Lake Taihu, respectively) when  $R$  was positive. The large GMR bias errors were attributed to the fact that the vapor  $\delta$  measurement had relative errors that were 3 to 10 times as large as relative errors in the concentration measurement for the IRIS instruments used in this study.

Previous studies on  $^{13}\text{C}$  showed that both the bias error and the random uncertainty of the Keeling intercept decrease with increasing concentration range. In the present study, increasing the water vapor concentration range reduced the standard error of the Keeling method using the YS and OLS regression, but had little effect on the bias error beyond the concentration range of about 200 ppm. On the other hand, the bias error was much smaller using two-height data (0.99‰ for YS and 0.44‰ for OLS, average of the two sites) than using one-height data (2.65‰ for YS and -0.34‰ for OLS) to perform the regression analysis.

The Keeling method with the OLS regression gave a slightly more robust estimate of  $\delta_E$  for Lake Taihu than the flux-gradient method under conditions of low vertical water vapor concentration gradient, when compared with the Craig-Gordon model prediction. This result requires further evaluation because it was based on a small sample size (82 hourly observations) and because high frequency variations (frequency greater than about 0.02 Hz) were filtered out by our measurement systems. A measurement system that samples the concentration and vapor delta sequentially between two or more heights and at the true eddy time scales may yield better results than shown in the present study.

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