

Yale 耶鲁大学-南京信息工程大学大气环境中心



Yale-NUIST Center on Atmospheric Environment

Validation of the Craig-Gordon isotopic model for lake evaporation

Wei Xiao

Yale-NUIST Center on Atmospheric Environment
Nanjing University of Information Science & Technology, Nanjing, China

**YNCenter Video Conference
Nanjing, China, May 3, 2013**

Outlines

1. Introduction
2. Model
3. Observation
4. Validation

1. Introduction

- The theory on isotopic composition of evaporation (δ_E) of open water was first proposed by Craig and Gordon in 1965 (C-G model) and has since been widely employed in studies of isotope hydrology and ecology.
- In a typical application, the interfacial surface water layer is assumed to be well-mixed so that the isotopic composition of the evaporating surface is equal to that of the bulk water.
- To date, the C-G model and the associated well-mixed assumption have not been validated against field measurements over natural water bodies.
- In this study, in-situ measurement of δ_E was made on a near-continuous basis using the flux-gradient approach over Lake Taihu, a large shallow lake in East China.

Background knowledge

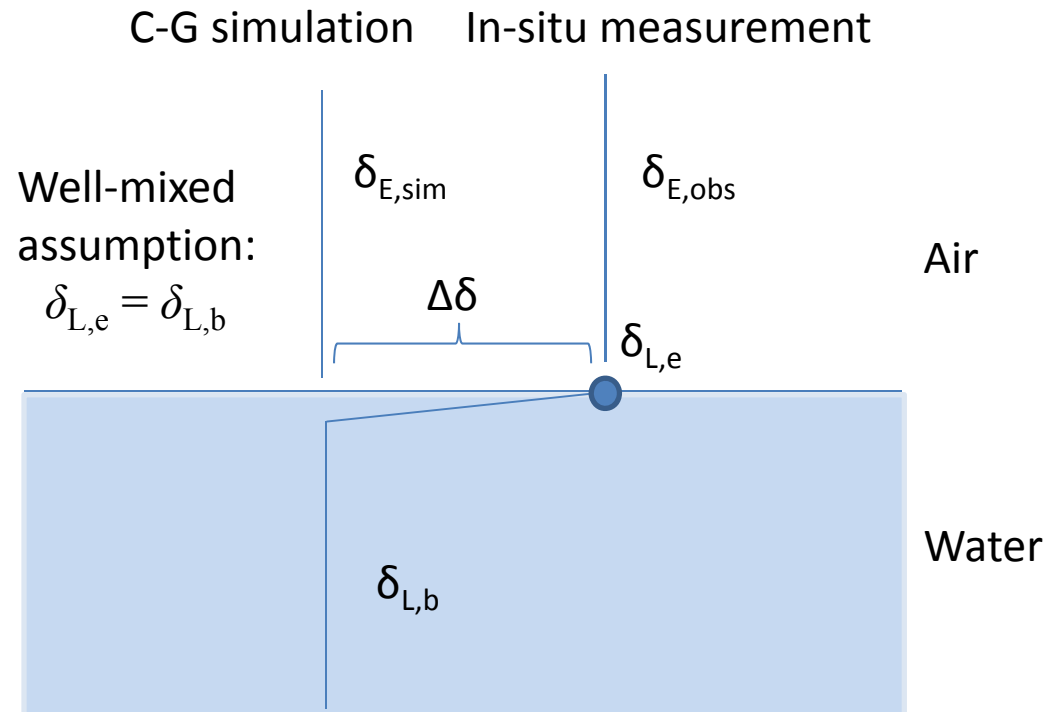
Vienna Standard Mean Ocean Water:

$$^{18}\text{O}/^{16}\text{O} = 2005.20 \pm 0.43 \text{ ppm}$$

$$^2\text{H}/^1\text{H} = 155.76 \pm 0.1 \text{ ppm}$$

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000, \text{‰}$$

Scientific hypothesis



$\delta_{E,sim} = \delta_{E,obs}$: well mixed
 $\delta_{E,sim} \neq \delta_{E,obs}$: not well mixed

2. Model

Craig-Gordon model:

$$\delta_E = \frac{\alpha_{eq}\delta_L - h\delta_a - \varepsilon_{eq} - (1-h)\varepsilon_k}{(1-h) + (1-h)\varepsilon_k \times 10^{-3}}$$

δ_E : isotopic composition of evaporation

δ_L : isotopic composition of lake water

δ_a : isotopic composition of atmospheric vapour

h : relative humidity reference to water surface temperature

ε_k : kinetic fractionation factor

ε_{eq} , α_{eq} : equilibrium fractionation factors

Equilibrium fractionation effect:

The fractionation factor between liquid (or solid) and vapor at equilibrium.

$$\alpha_{eq} = \left(\frac{R_{liquid}}{R_{vapor}} \right)_{eq} = \frac{p_{H_2O}^{16}}{p_i} = 1 + \varepsilon_{eq}$$

p_i : saturation vapor pressure of HDO or $H_2^{18}O$

$$\alpha_{eq,O} = \exp \left(\frac{1.137 \times 10^3}{T_s^2} - \frac{0.4156}{T_s} - 2.0667 \times 10^{-3} \right)$$

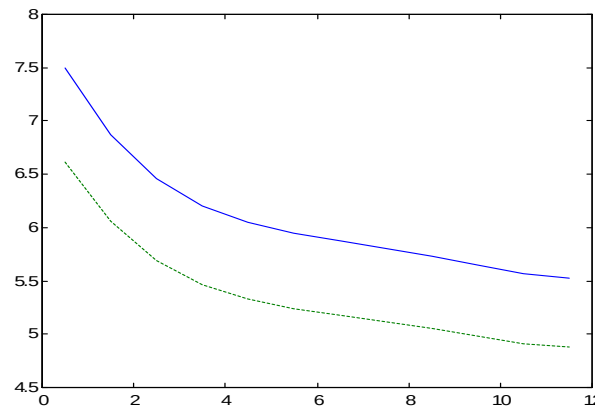
$$\alpha_{eq,D} = \exp \left(\frac{24.844 \times 10^3}{T_s^2} - \frac{76.248}{T_s} + 52.612 \times 10^{-3} \right)$$

(Majoube 1971)

Kinetic fractionation effect:

Due to different molecular diffusion rate of the heavier (HDO and H_2^{18}O) molecules and the lighter (H_2^{16}O) molecules at the air-liquid interface.

The determination of ε_k requires the characterization of the degree of molecular and turbulent diffusion.



Regression fit to the kinetic fractionation factors produced by the Merlivat and Jouzel smooth regime model for evaporation from a water surface

$$\varepsilon_{k,O} = 4.6351u^4 \times 10^{-4} - 0.01465u^3 + 0.1696u^2 - 0.9261u + 7.9230$$

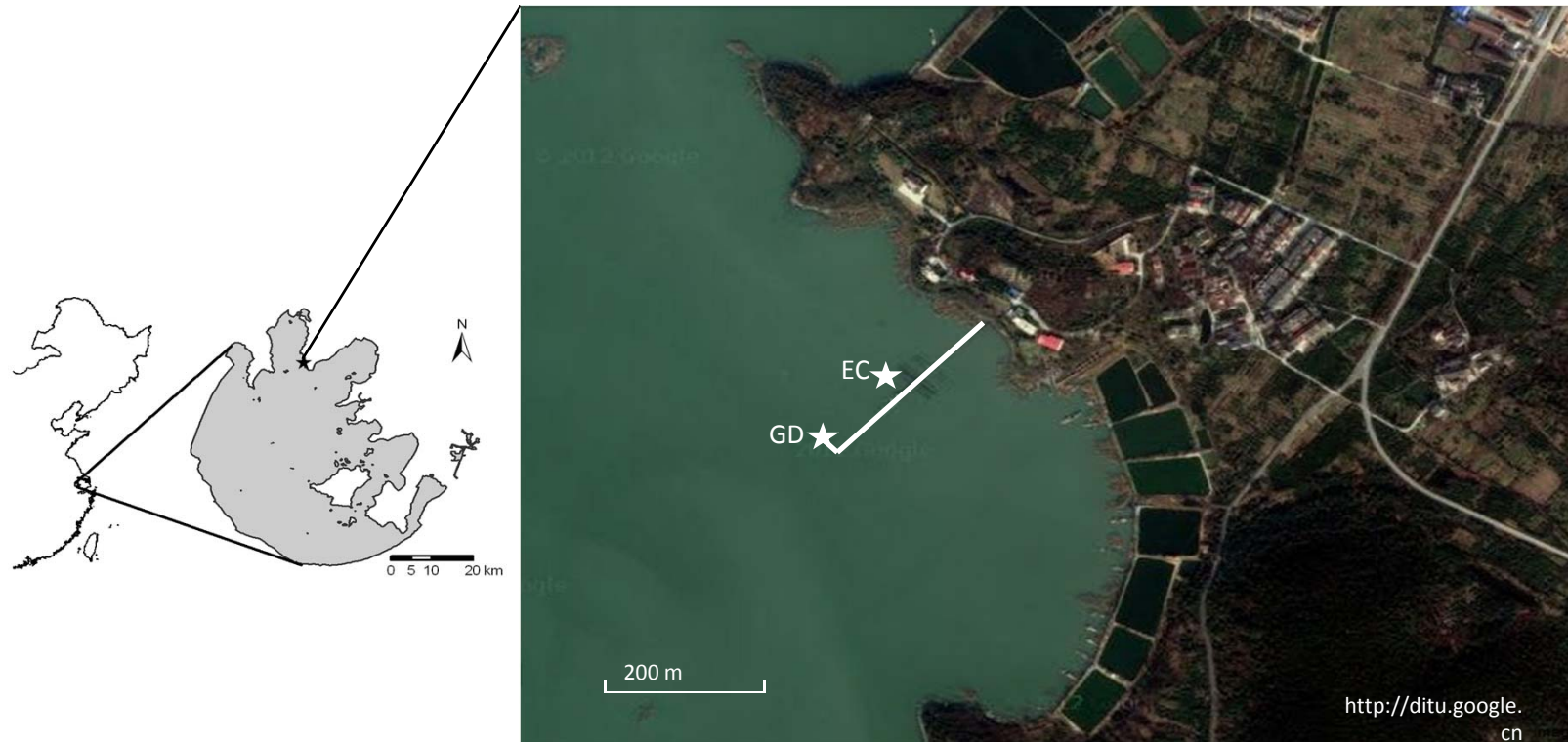
$$\varepsilon_{k,D} = 4.0917u^4 \times 10^{-4} - 0.01293u^3 + 0.1497u^2 - 0.8174u + 6.9882$$

(Merlivat and Jouzel, 1979)

- 3.1 Experimental site
- 3.2 Instrument
- 3.3 Schematic design diagram
- 3.4 Instrument performance
- 3.5 Data screening
- 3.6 Calibration methods

3. OBSERVATION

3.1 Experimental site

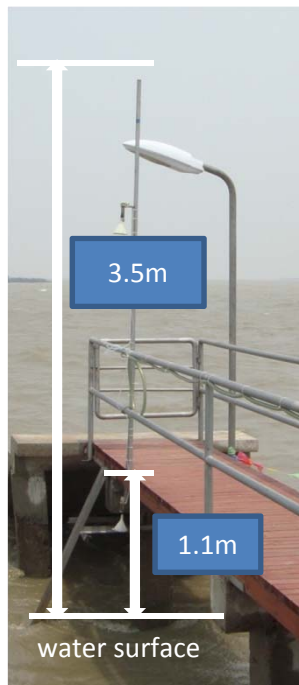


The experiment site ($31^{\circ}24'N$, $120^{\circ}13'E$) was in the north part of Lake Taihu, which is the third largest freshwater lake in China, with a water surface area of 2400 km^2 and a mean water depth of 1.9 m

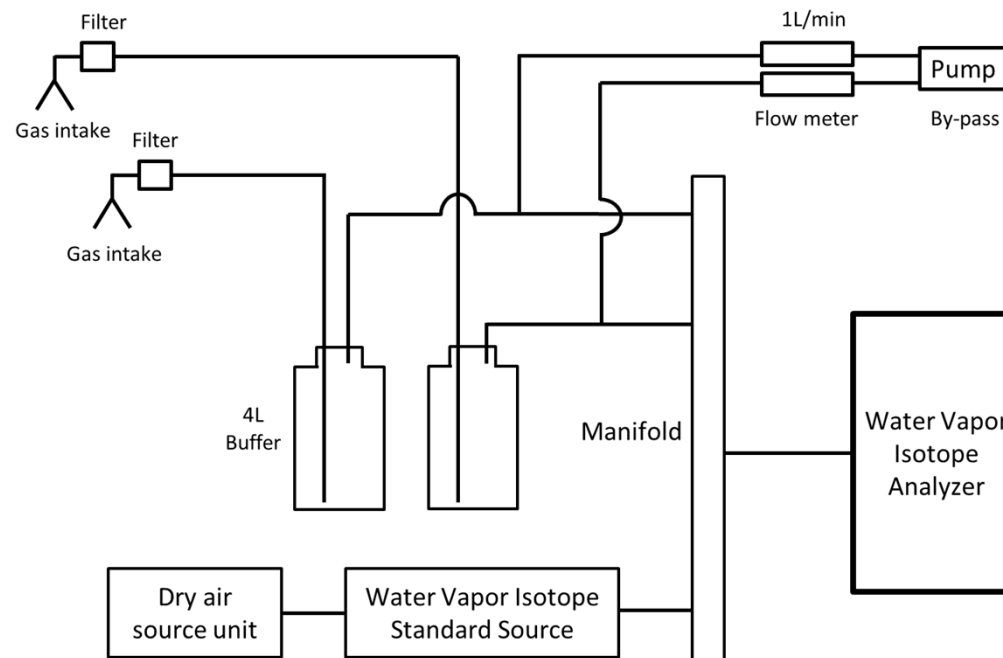
3.2 Instrument



- The key instrument was a water vapor analyzer based on the off-axis integrated cavity output spectroscopy.
- The analyzer switched between the two intakes at the 1.1 and 3.5 m height above water surface every 30s, measuring the H_2^{16}O , HDO and H_2^{18}O water vapor mixing ratios.



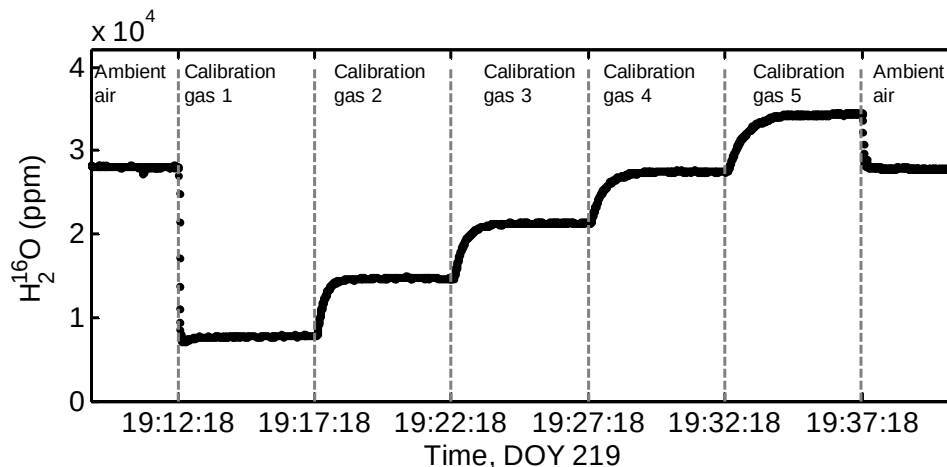
3.3 Schematic Design Diagram



The flux-gradient method was used to obtain the isotopic compositions of lake evaporation. Buffer volumes were used to improve the accuracy of the gradient measurement. Small short tubing was used between the manifold and the analyzer to minimize the transient time between valve switching.

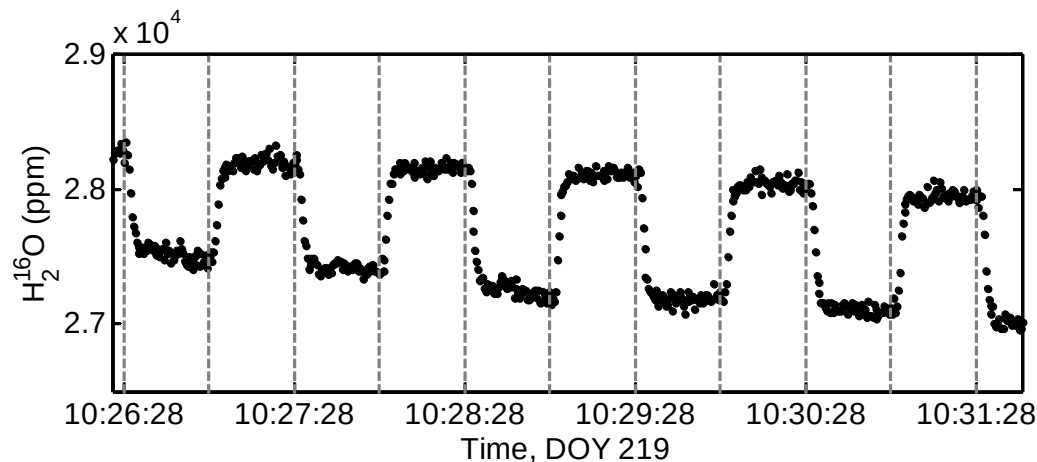
3.4 Instrument Performance (1/2)

Calibration gases:



To eliminate the effect of non-linearity and signal drift, we calibrated the analyzer every 3 h against 5 water vapor standards of identical isotopic compositions.

Ambient air:



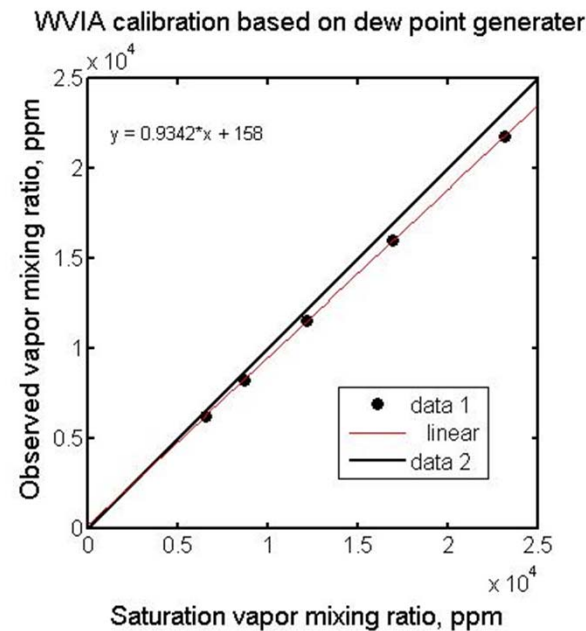
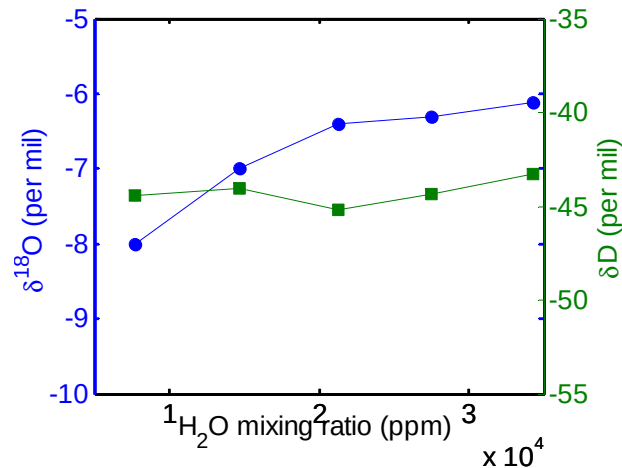
When measuring the ambient air, the manifold switched between the two intakes every 30 s.

The measurement approached steady state in less than 10 s after each switching.

3.4 Instrument Performance (2/2)

Non-linearity & calibration

The analyzer displayed nonlinear behavior. The measured $\delta^{18}\text{O}$ and δD of the calibration gases ranged from -8.0 to -6.1‰ and -45.2 to -43.3‰, respectively. The true values were -7.0‰ and -44.0‰, respectively.



3.5 Data screening

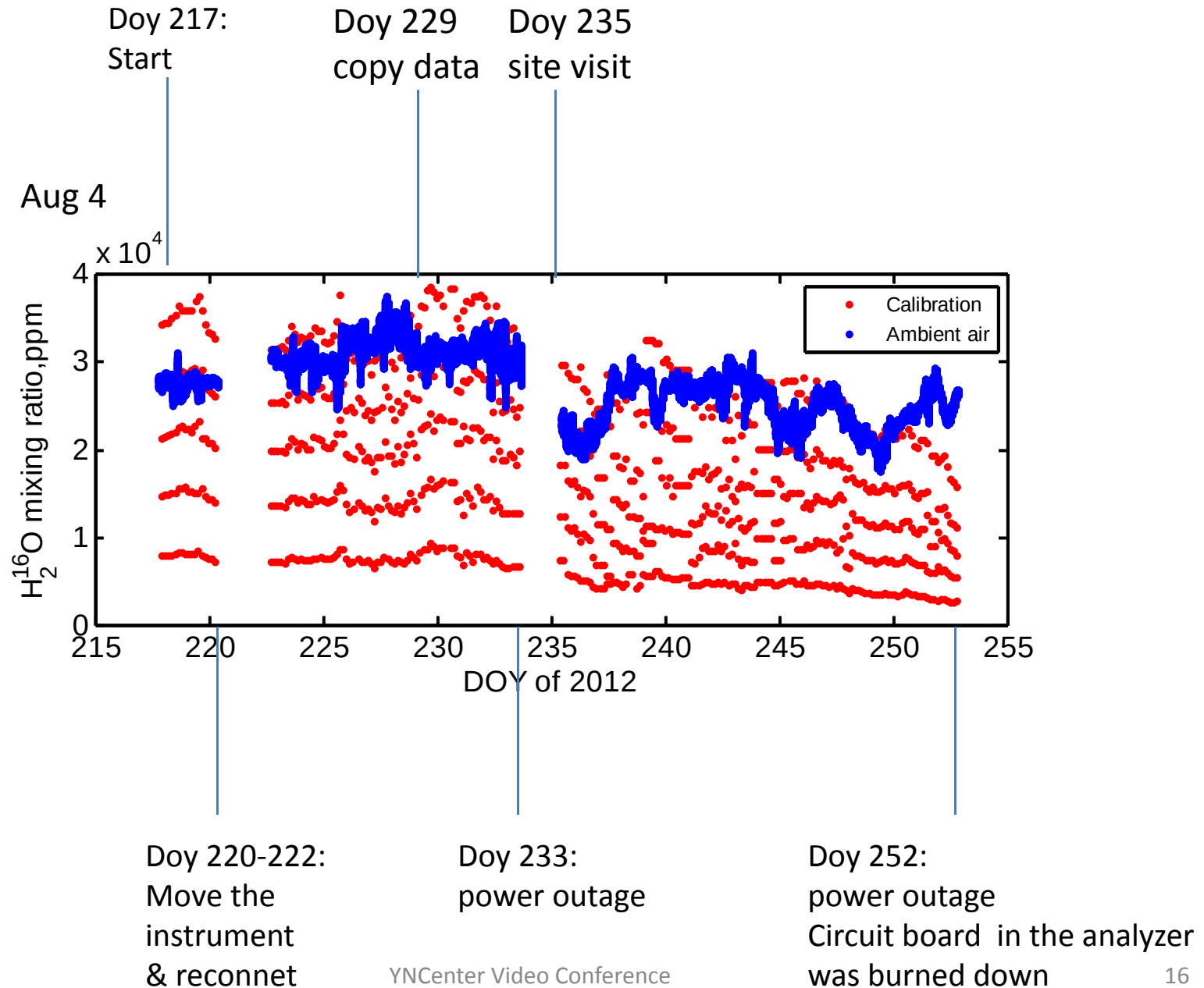
We encountered a lot of problems during the experiment:

- power outage,
- blocked microdrop generator,
- broken standard source,
- dirty filters,
- broken dry air source unit,
- burned circuit board,
- unstable routine etc.

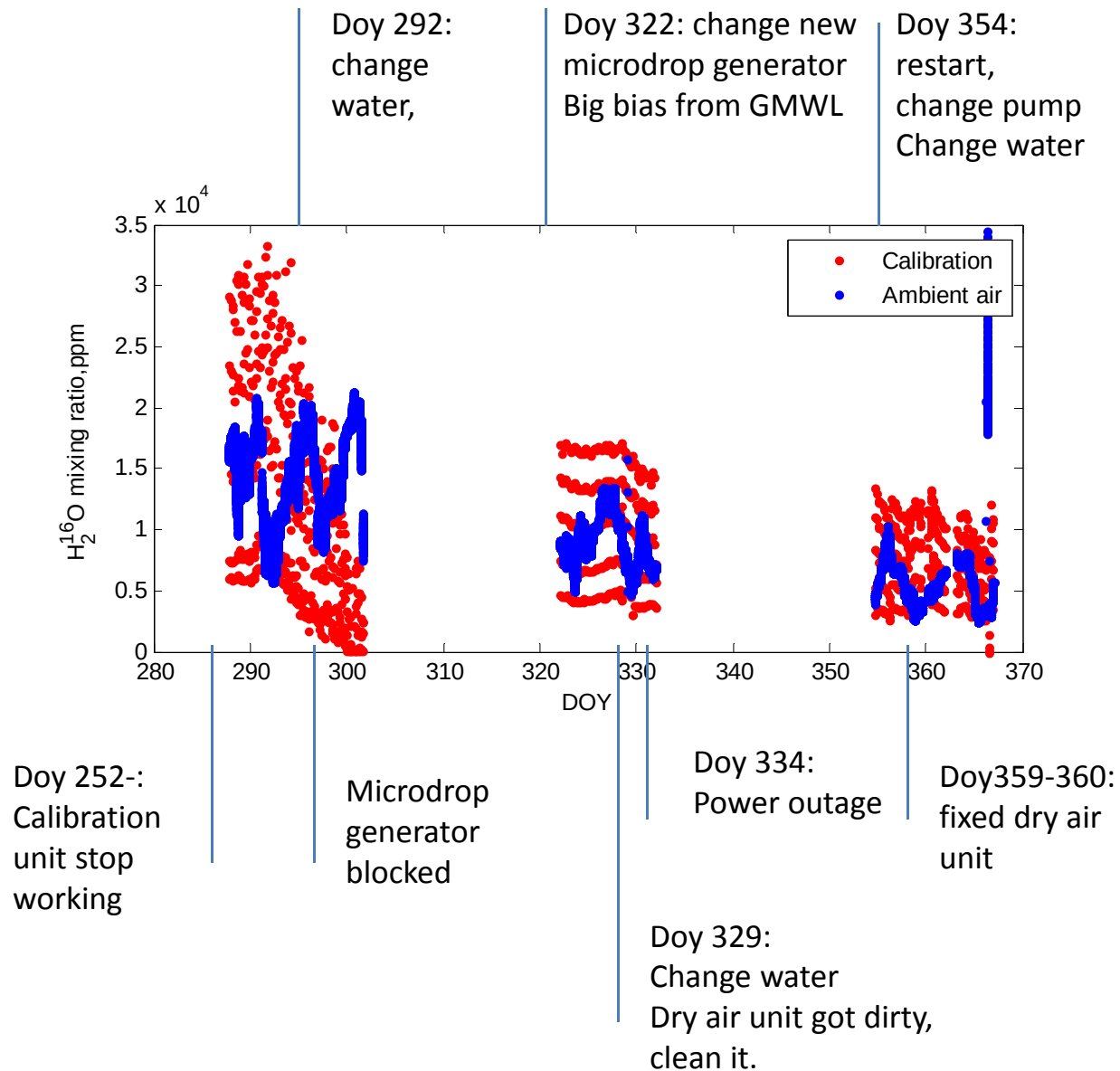
I selected observation with good calibration gases manually and removed data with big bias from GWML.

only < 25% data are useful!

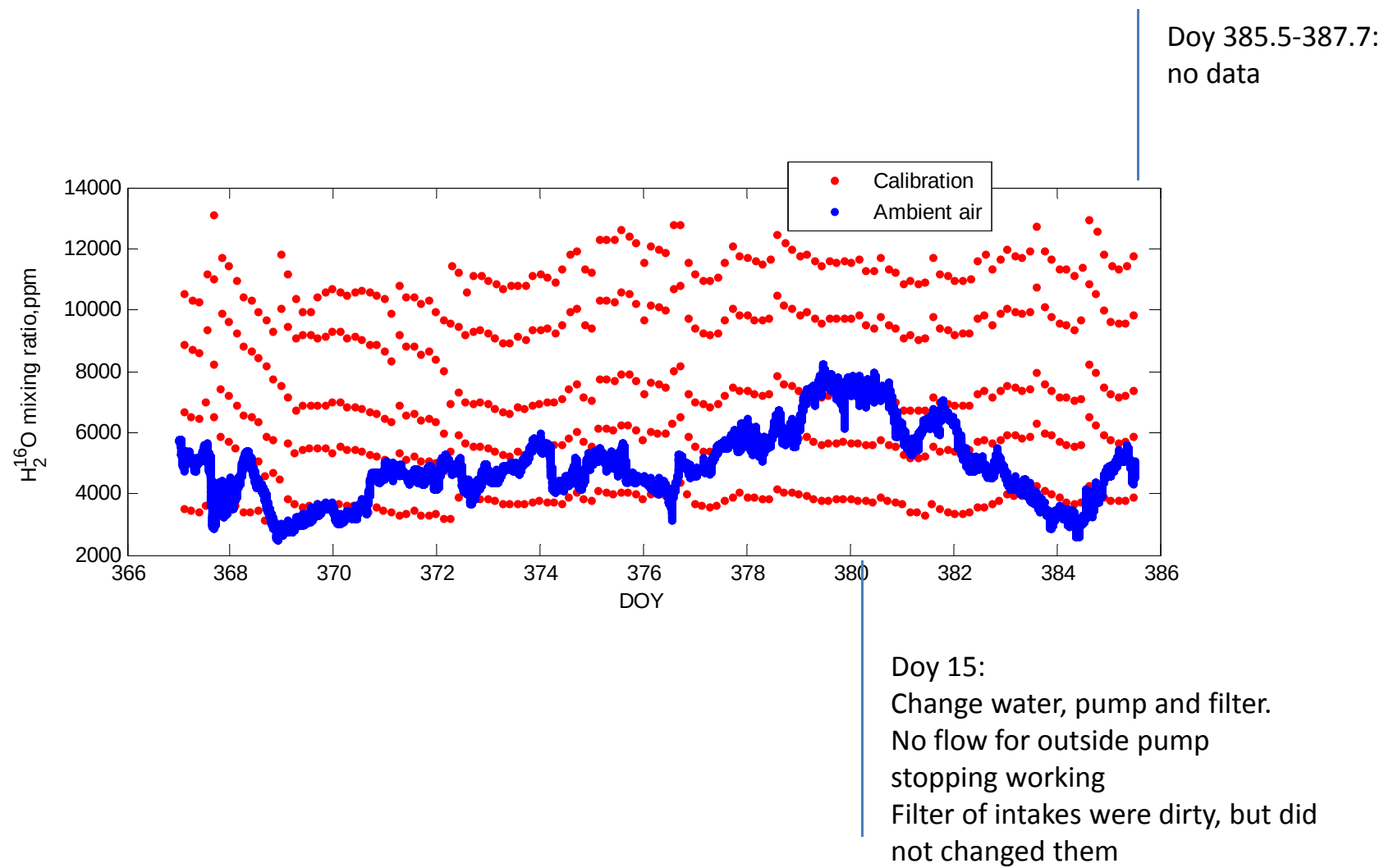
Aug 4 - Sep 8, 2012



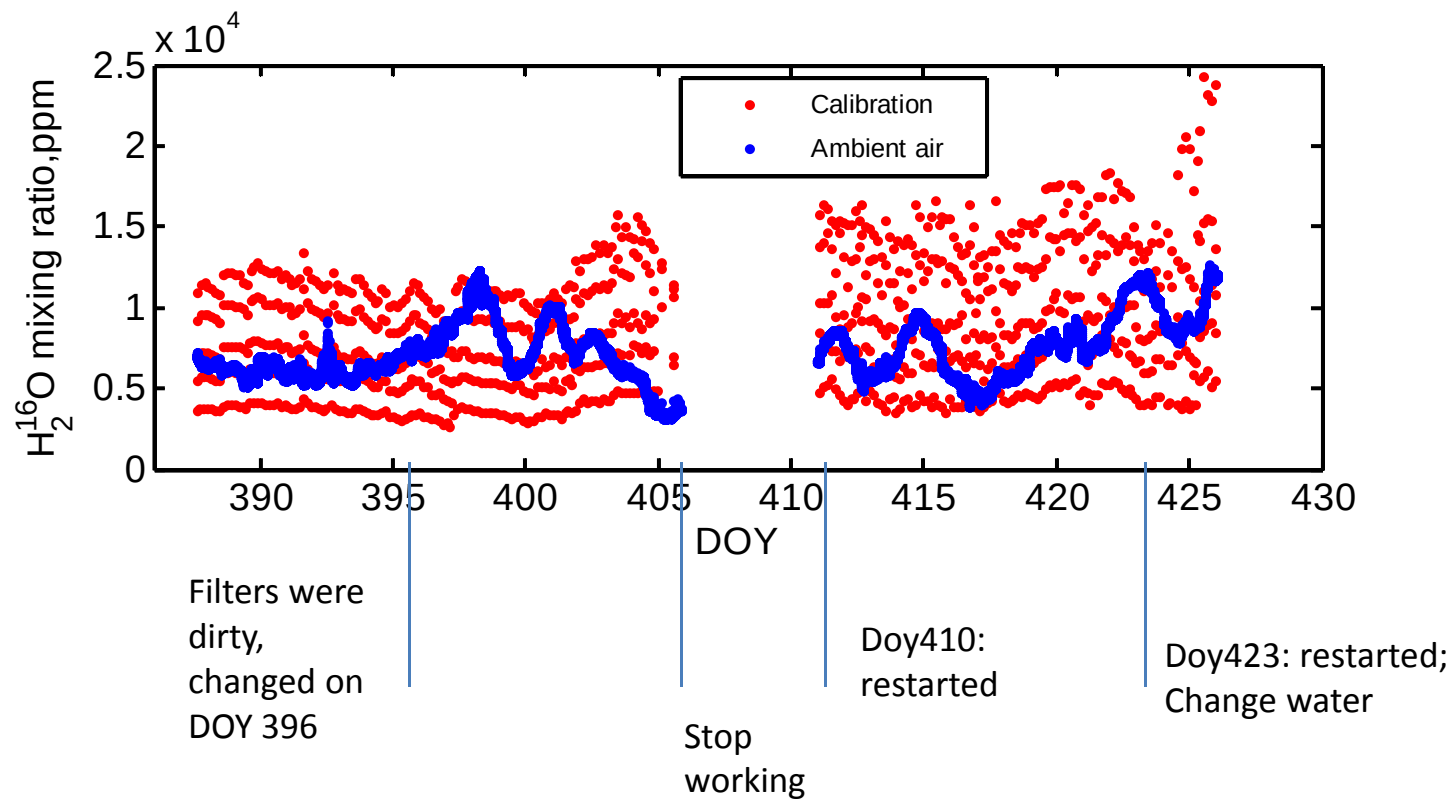
Oct 14 – Dec31, 2012



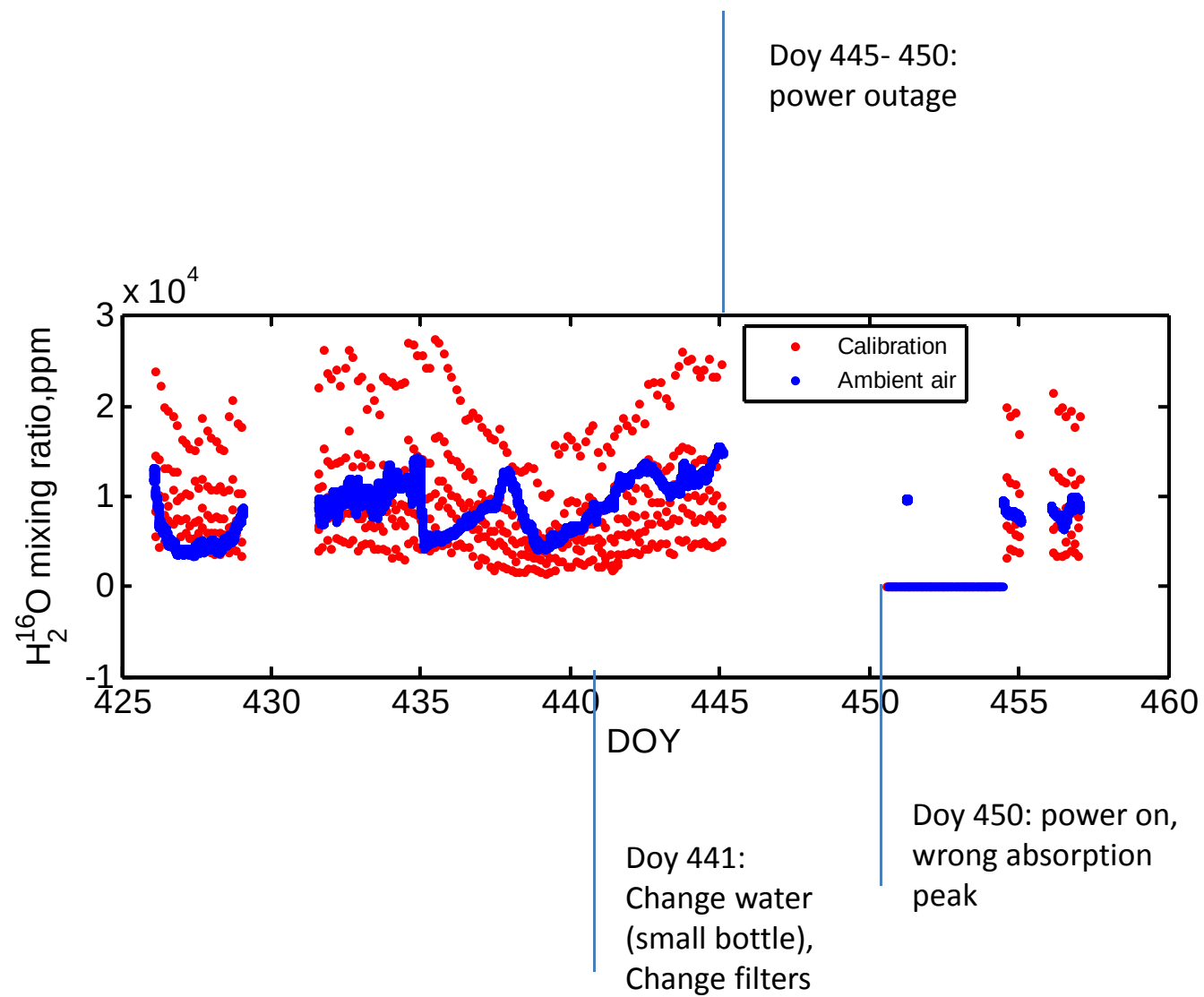
Jan 1-20, 2013



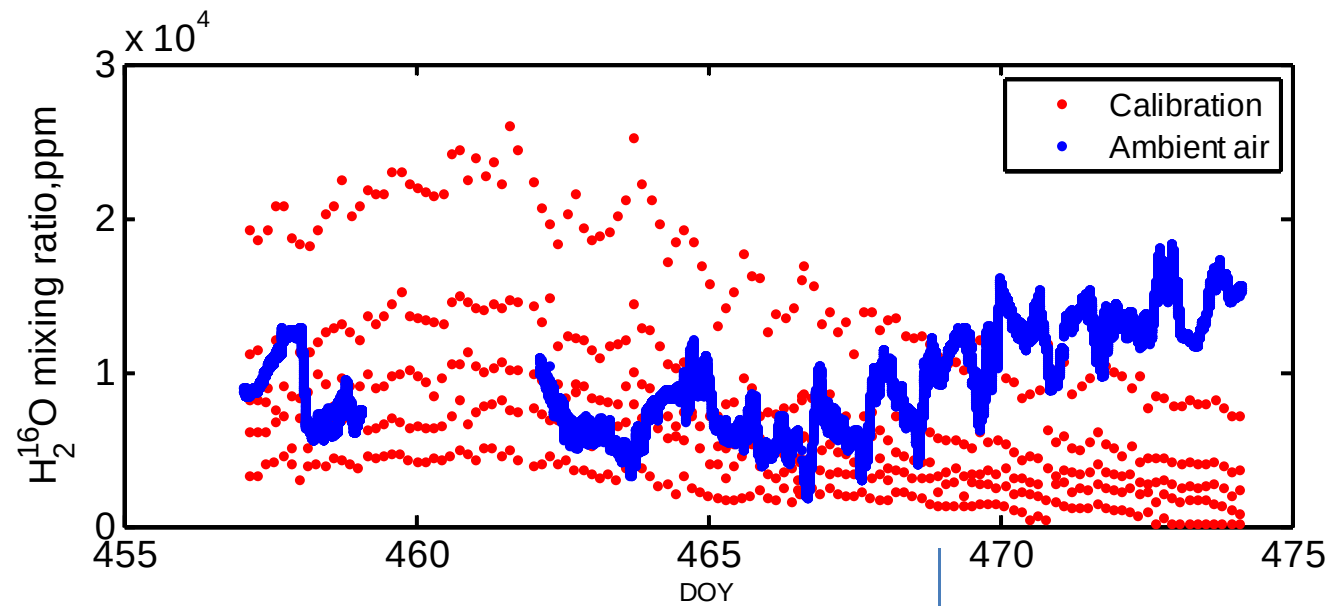
Jan 21 - Feb 28, 2012



March 1 – 31, 2013



April 1-17, 2013



Microdrop
generator blocked

3.6 Calibration methods

For the isotopic composition of atmospheric water vapor:

$$R_a = R_1 + \frac{R_2 - R_1}{x_{s,2}^0 - x_{s,1}^0} \cdot (x_a^0 - x_{s,1}^0)$$

$$R_1 = R_c \cdot \frac{x_{s,1}^0}{x_{s,1}'} \cdot \frac{x_a'}{x_a^0} \quad R_2 = R_c \cdot \frac{x_{s,2}^0}{x_{s,2}'} \cdot \frac{x_a'}{x_a^0}$$

For the isotopic composition of evaporation:

$$R_E = R_d \cdot \frac{x_{s,2}^0 - x_{s,1}^0}{x_{s,2}' - x_{s,1}'} \cdot \frac{x_{a,2}' - x_{a,1}'}{x_{a,2}^0 - x_{a,1}^0}$$

(Lee et al. 2007)

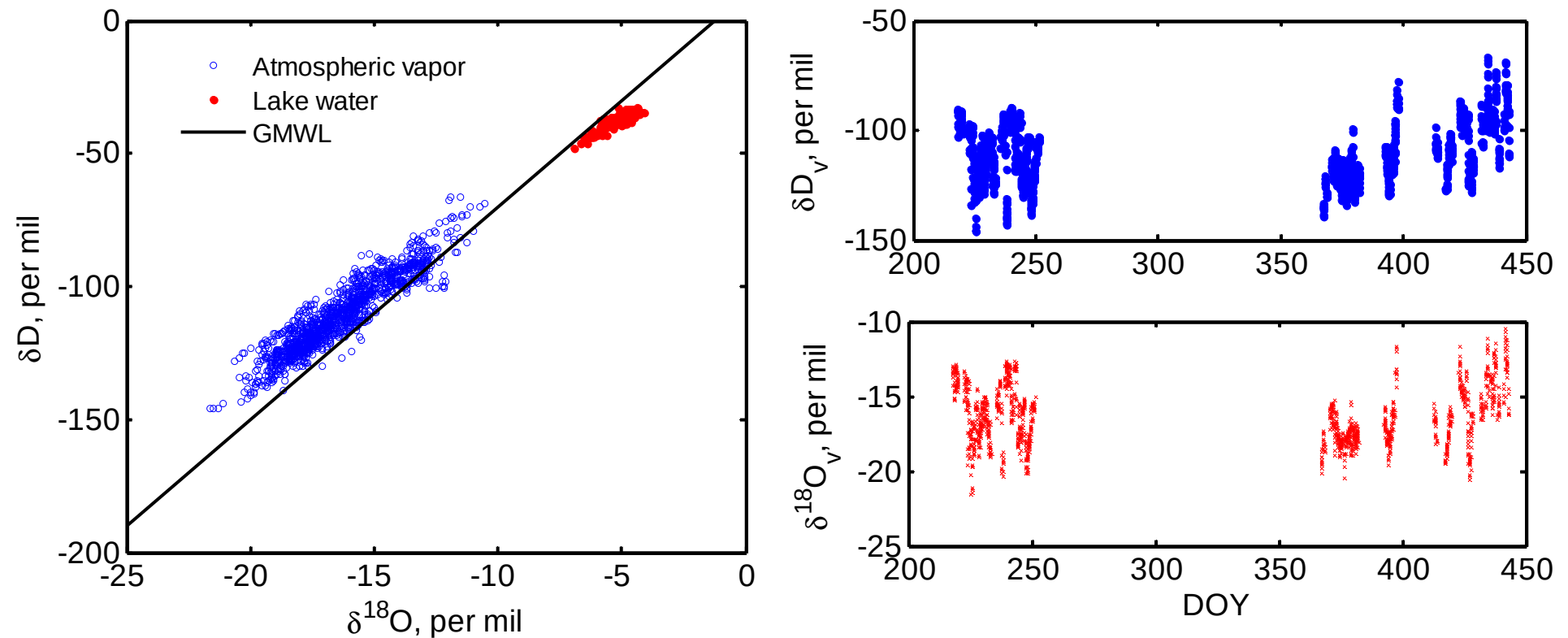
4.1 Inputs variables

4.2 Intermediate variables

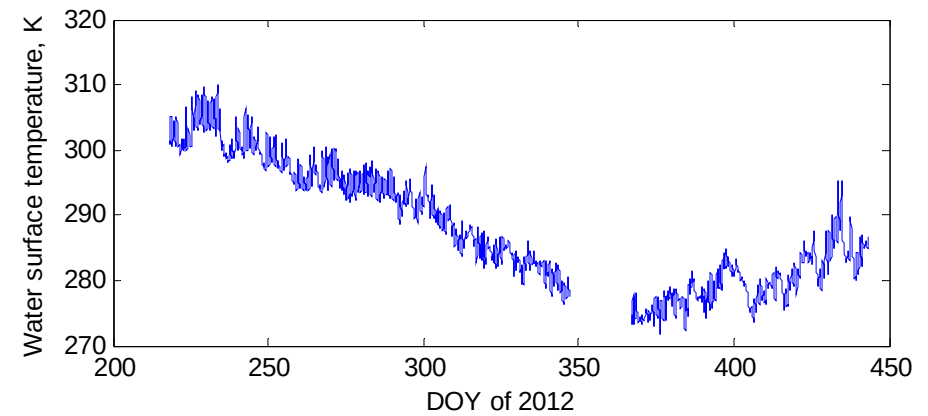
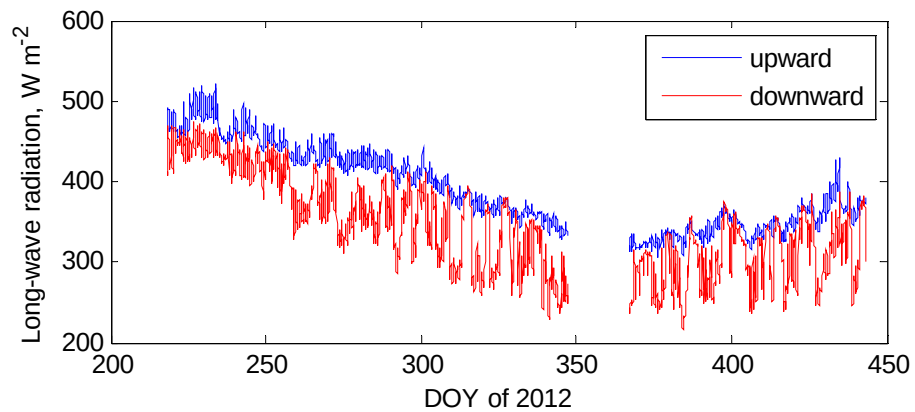
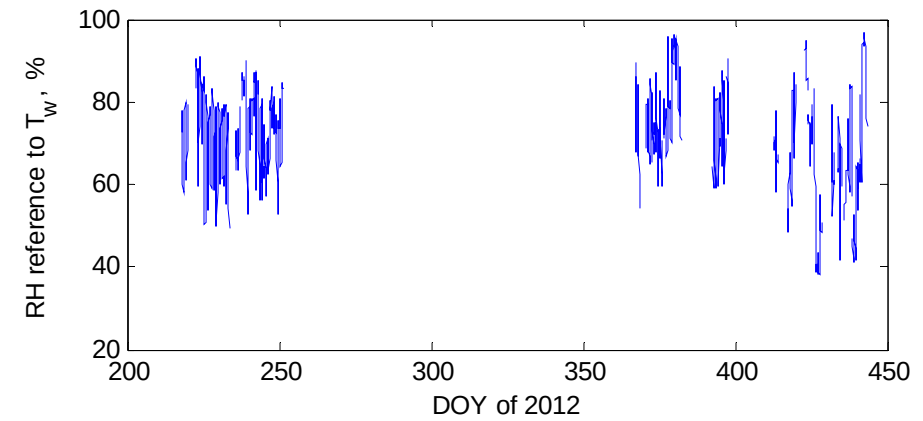
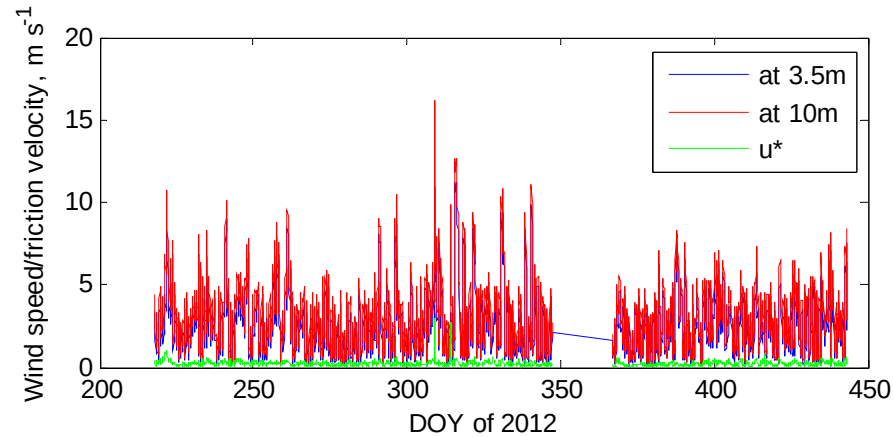
4.2 output variables

4. VALIDATION OF CG MODEL

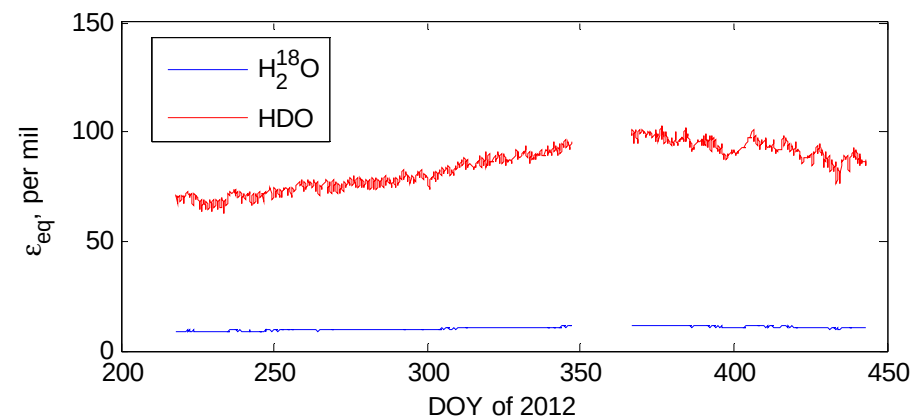
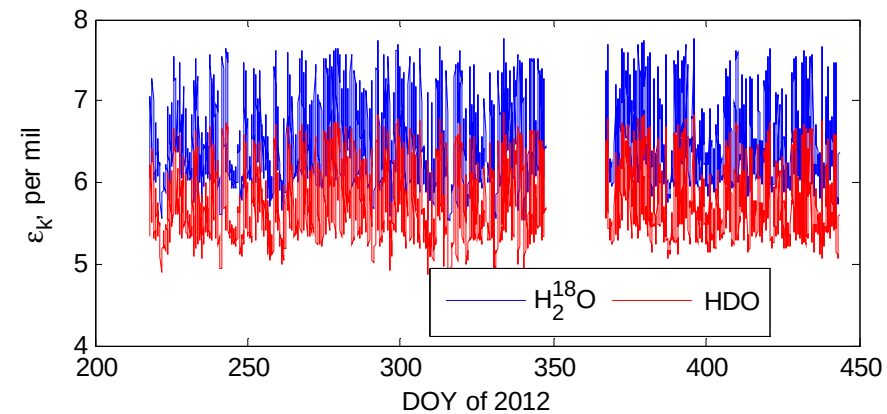
4.1 Input variables (1/2)



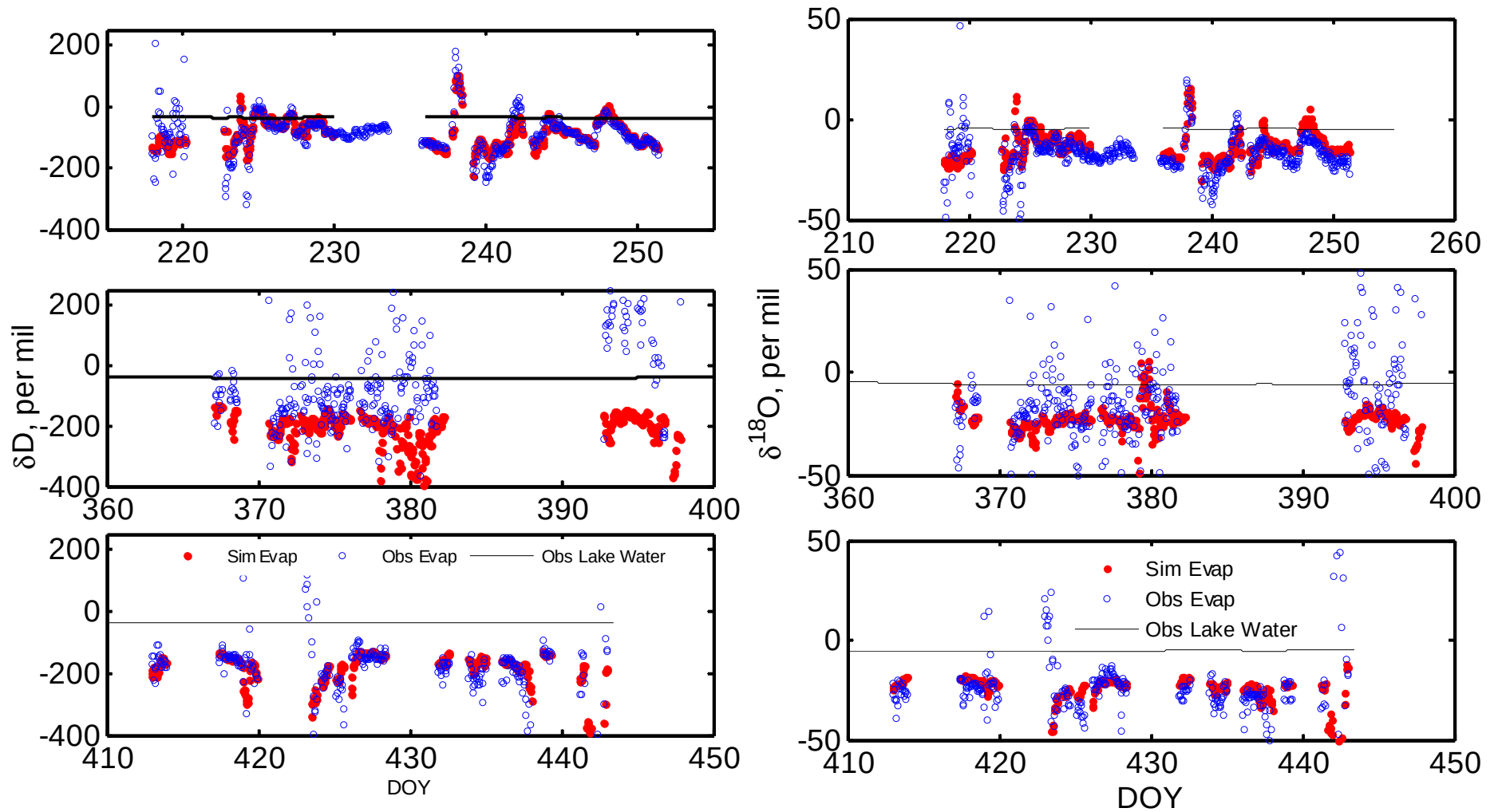
4.1 Input variables (2/2)



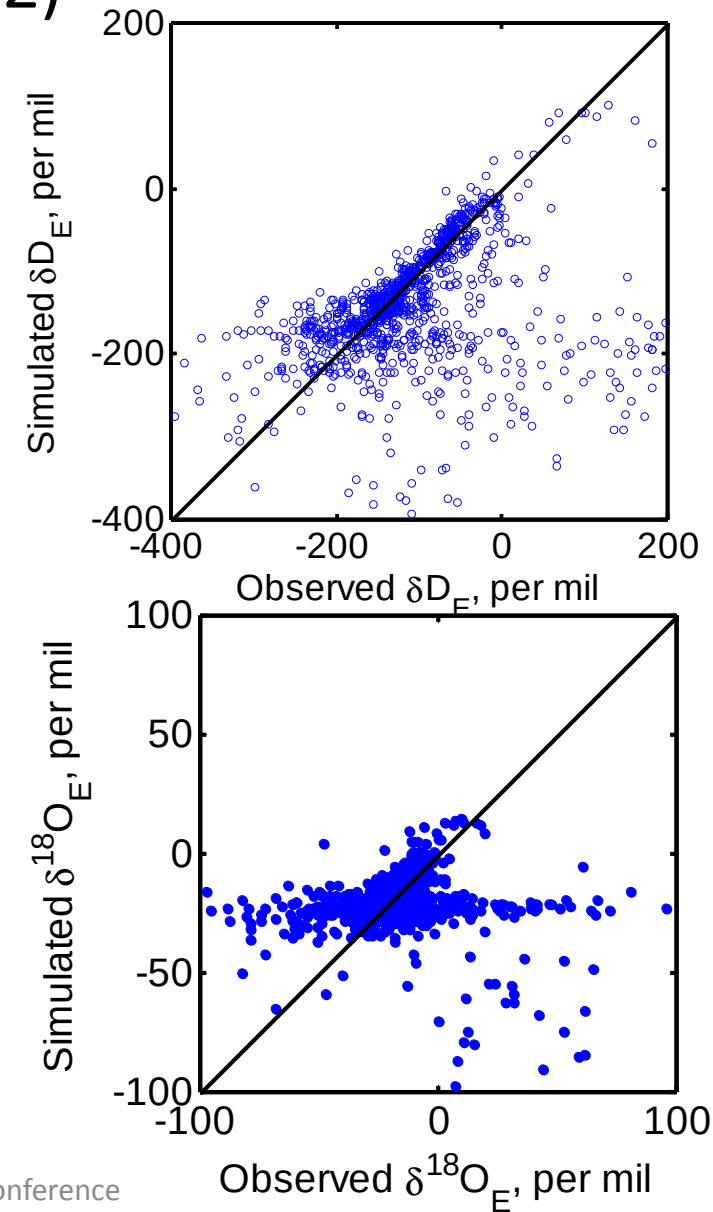
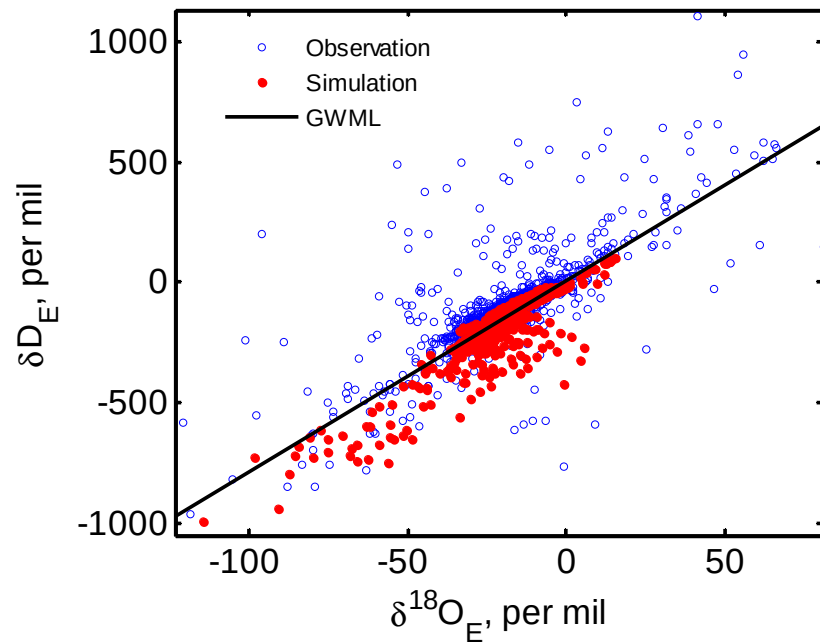
4.2 Fractionation factors



4.3 δ value of evaporation (1/2)



4.3 δ value of evaporation (2/2)



Acknowledgement

- Professor Xuhui Lee
- Professor Xuefa Wen
- Professor Shoudong Liu
- Hanchao Li, M.S. Candidate
- Cheng Hu , M.S. Candidate
- Yunqiu Gao , M.S. Candidate
- Qitao Xiao , M.S. Candidate
- Jing Shen , M.S. Candidate
- Yangzhou Wu , M.S. Candidate
- Cheng Liu , M.S. Candidate

