Yale 耶鲁大学-南京信息工程大学大气环境中心

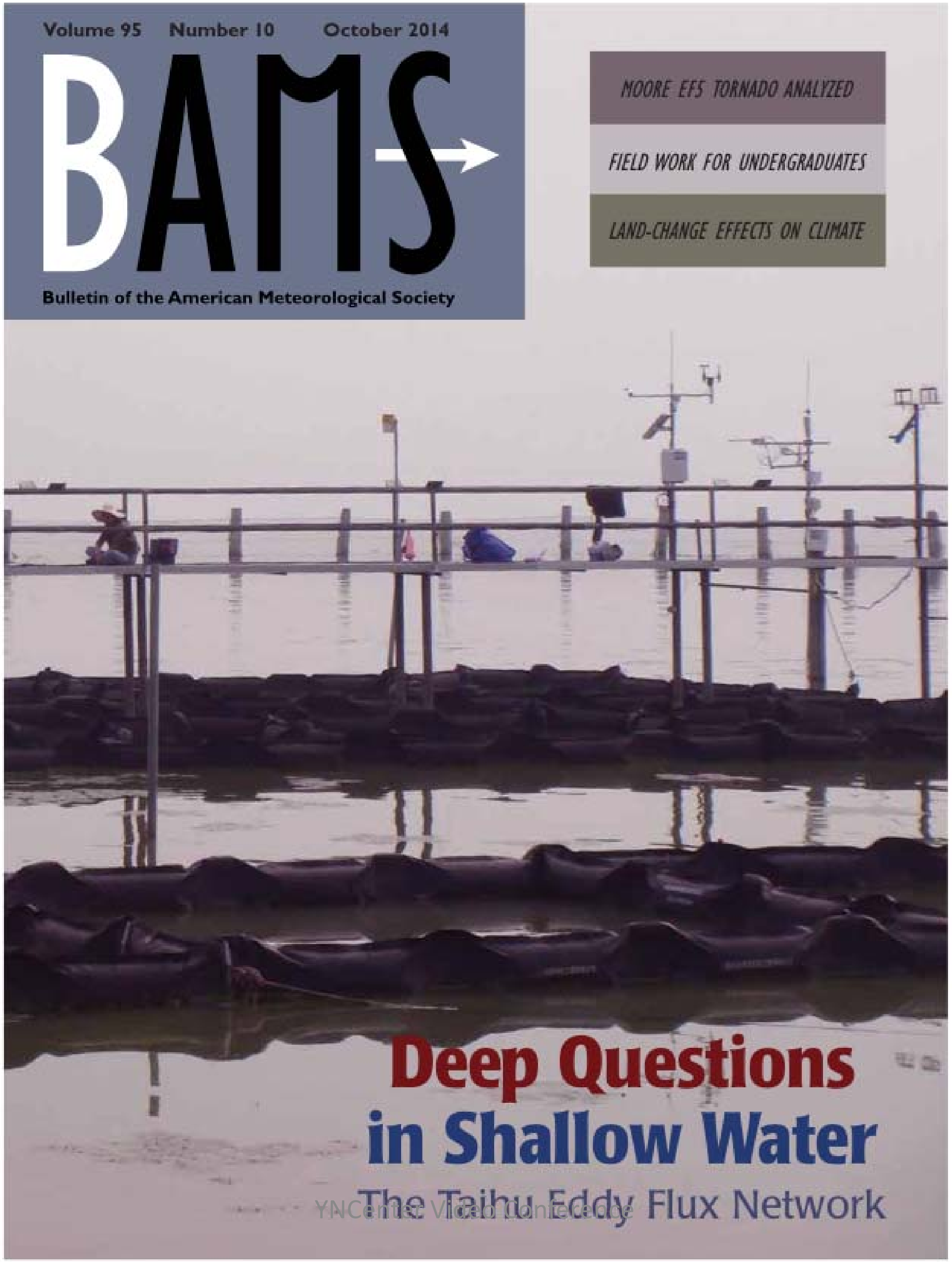
Yale-NUIST Center on Atmospheric Environment

Hydrogen and oxygen isotope compositions of lake water and evaporation

Wei Xiao

YNCenter Video Conference

April 23, 2015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BAMS
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MOORE EF5 TORNADO ANALYZED
FIELD WORK FOR UNDERGRADUATES
LAND-CHANGE EFFECTS ON CLIMATE
Deep Questions
in Shallow Water
The Taihu Eddy Flux Network

Outline

- Background information
- Lake water isotope
  - Lake and river survey
  - Spatial patterns and seasonality
- Isotopic lake evaporation
  - Craig-Gorden model
  - In-situ measurement
  - Model validation
- Isotopic mass balance method
  - Theory
  - Results

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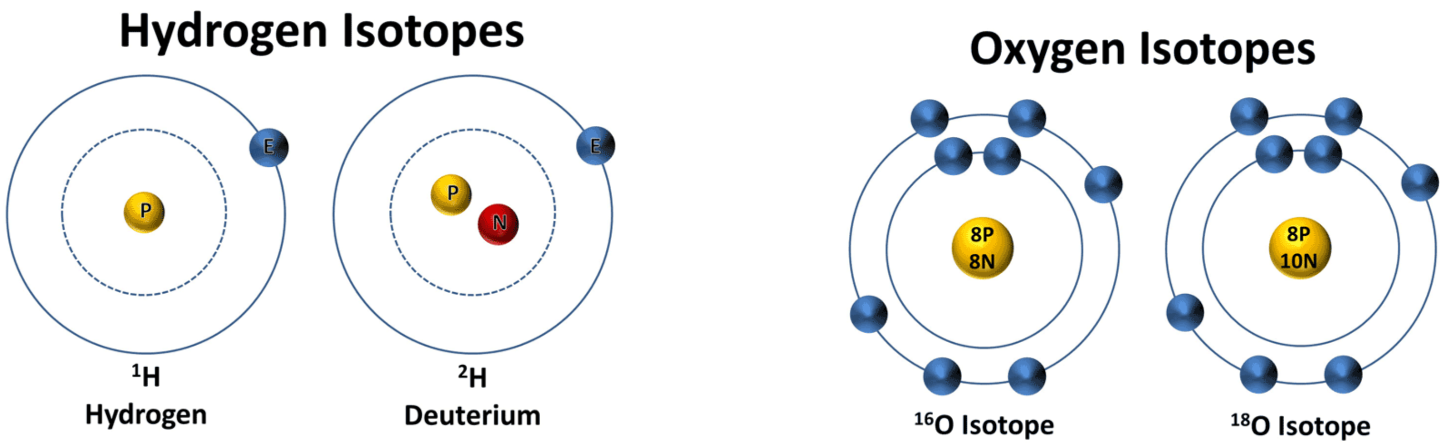
Isotopes in water



Vienna Standard Mean Ocean Water (VSMOW)

$^{2}H/^{1}H = 155.76 \pm 0.1$ ppm (a ratio of 1 part per approximately 6420 parts)

$^{18}O/^{16}O = 2005.20 \pm 0.43$ ppm (a ratio of 1 part per approximately 498.7 parts)

$$\delta = \left(\frac{R_{sample}}{R_{s\tan dard}} - 1 \right) \times 1000, ‰$$

Global Meteoric Water Line

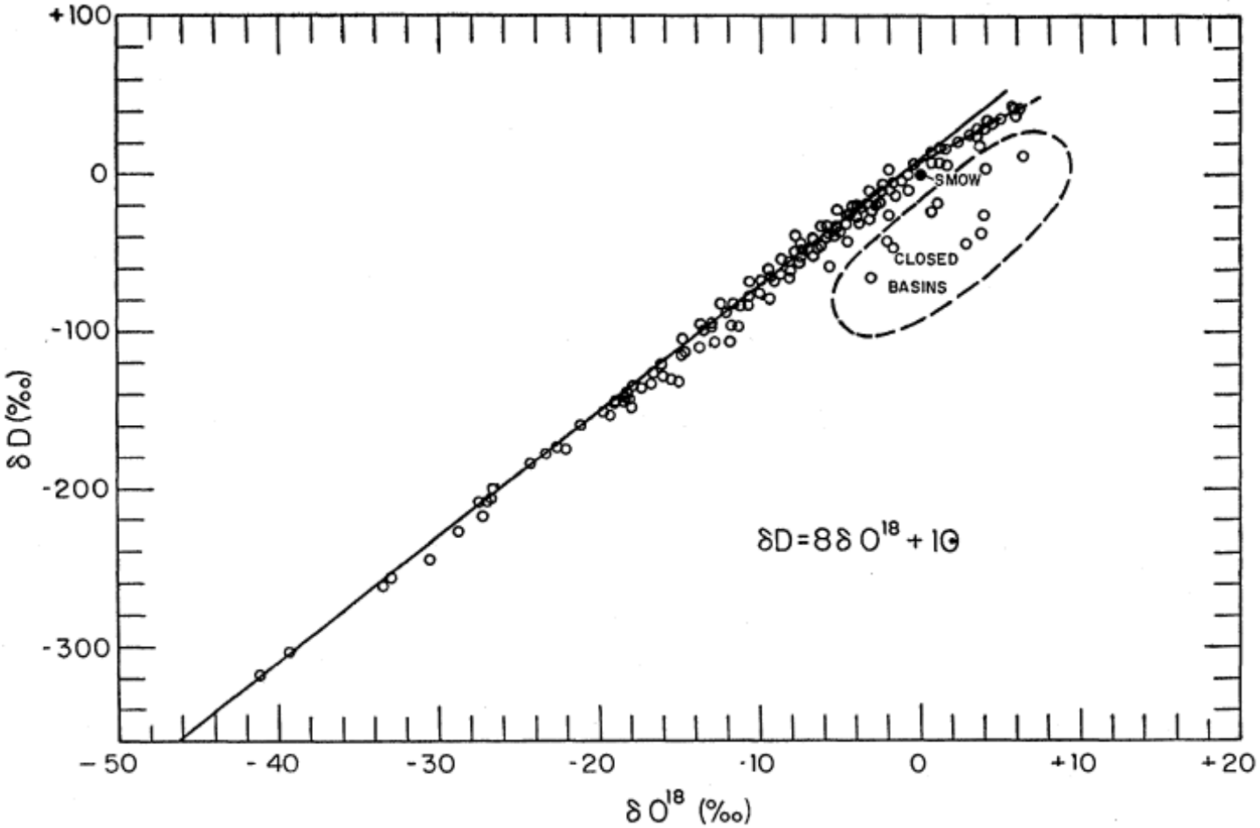


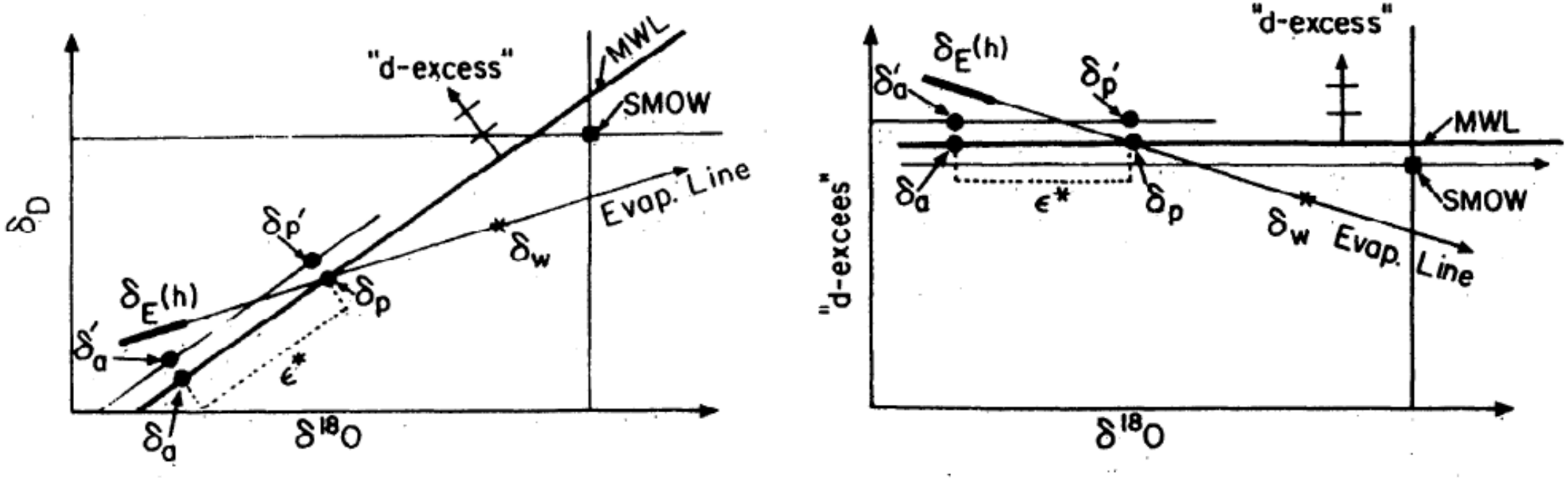
Fig. 1. Deuterium and oxygen-18 variations in rivers, lakes, rain, and snow, expressed as per millage enrichments relative to "standard mean ocean water" (SMOW). Points which fit the dashed line at upper end of the curve are rivers and lakes from East Africa.

400 samples of water from rivers, lakes, and precipitation.

(Craig 1961)

Deuterium-excess （过量氘）

$$d = \delta D - 8\ \delta^{18}O$$



Rainout: invariant with respect to the *d-excess*.

Transpiration: no change in the *d-excess*.

Evaporation: The evaporated waters usually have a higher *deuterium-excess* value.

(Dansgaard 1964; Gat et al. 1994)

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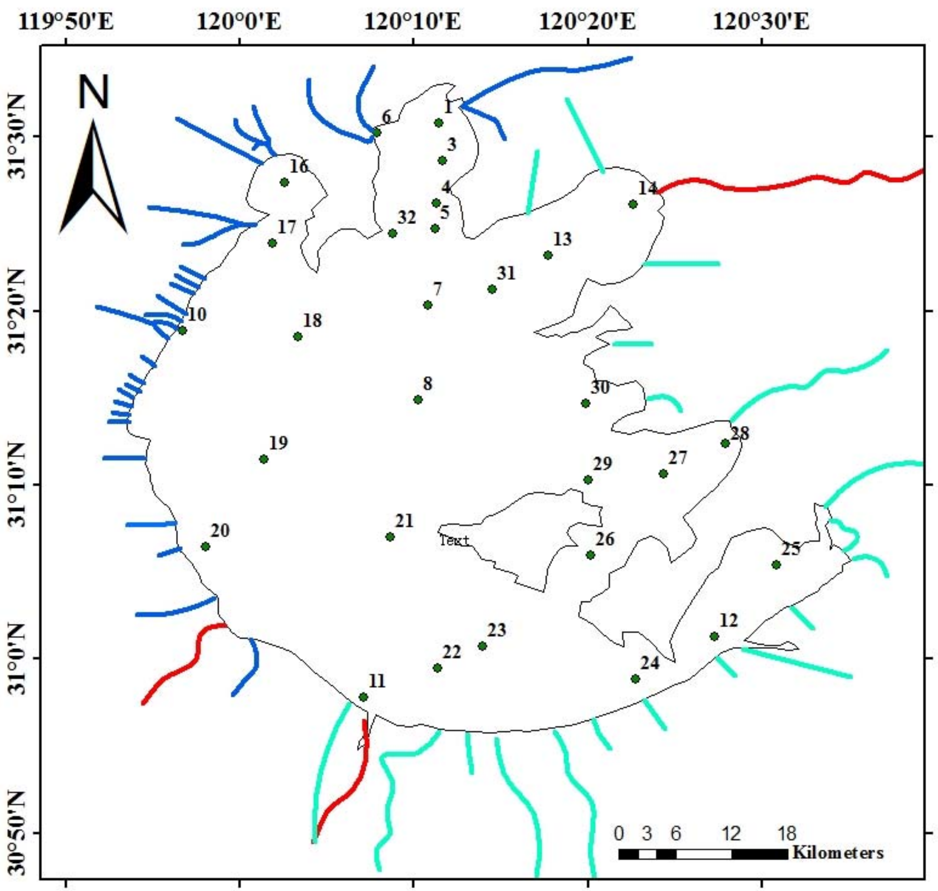
Lake and river surveys



Dots: lake survey sites   Blue: inflow rivers

Green: outflow rivers   Red: inflow/outflow rivers

Whole-lake survey:

29 sites

Since August 2011

Seasonally (Feb, May, Aug, Nov)

River survey:

51 rivers

27 inflow rivers

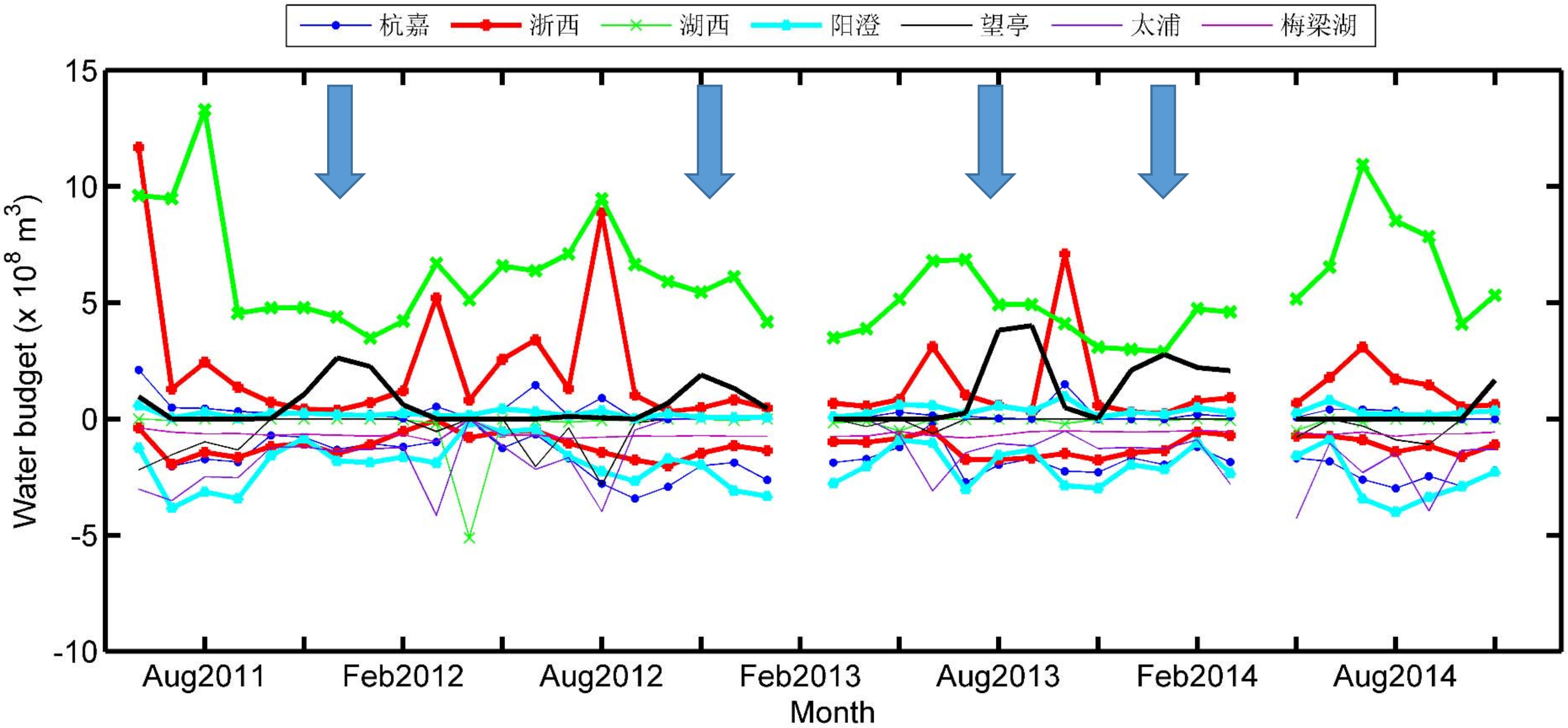
21 outflow rivers

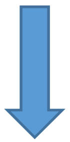
3 inflow/outflow rivers

Since May 2013

Seasonally (Feb, May, Aug, Nov)

Inflow and outflow water budget of Lake Taihu



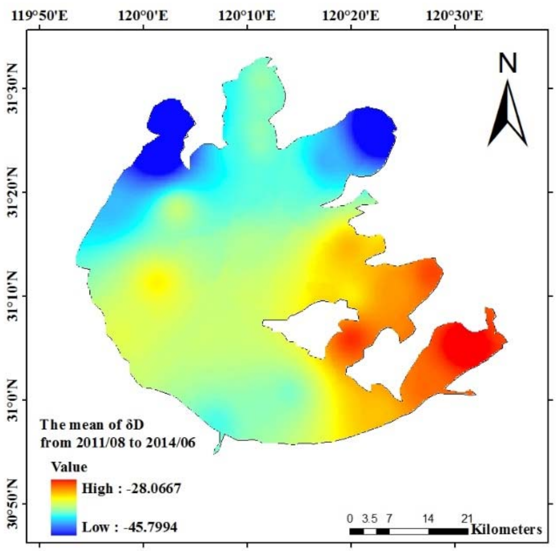


Water diversion from Yangze river to Lake Taihu（引江济太）

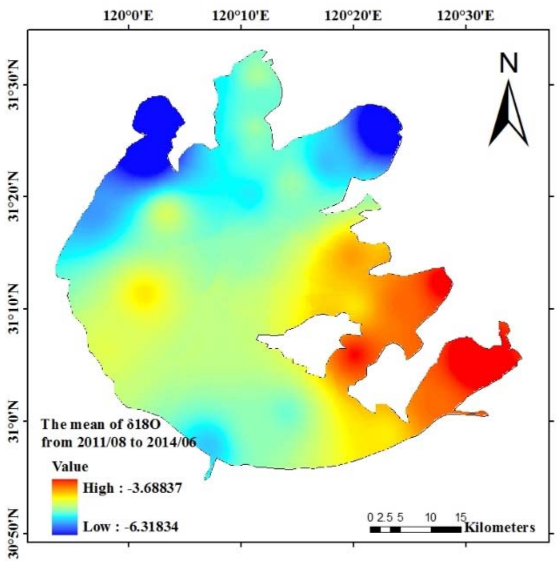
http://www.tba.gov.cn/

Seasonal mean spatial patterns of the lake water isotope

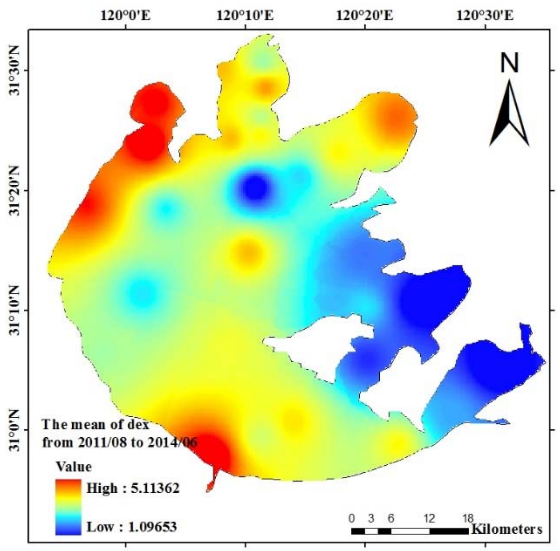
δD_L



$\delta^{18}O_L$



d_L

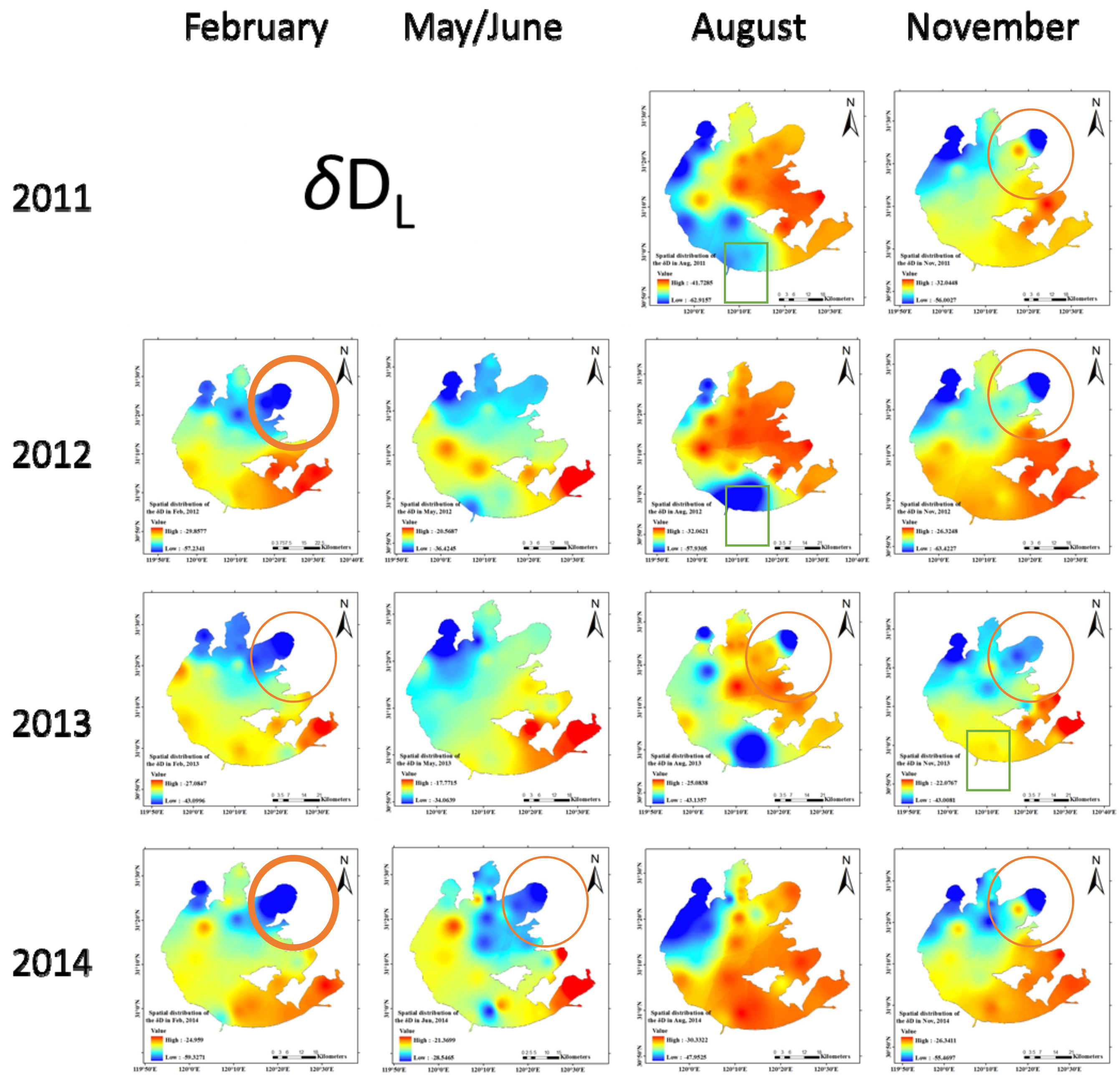


Inflow region: lower δD_L and $\delta^{18}O_L$, higher d_L

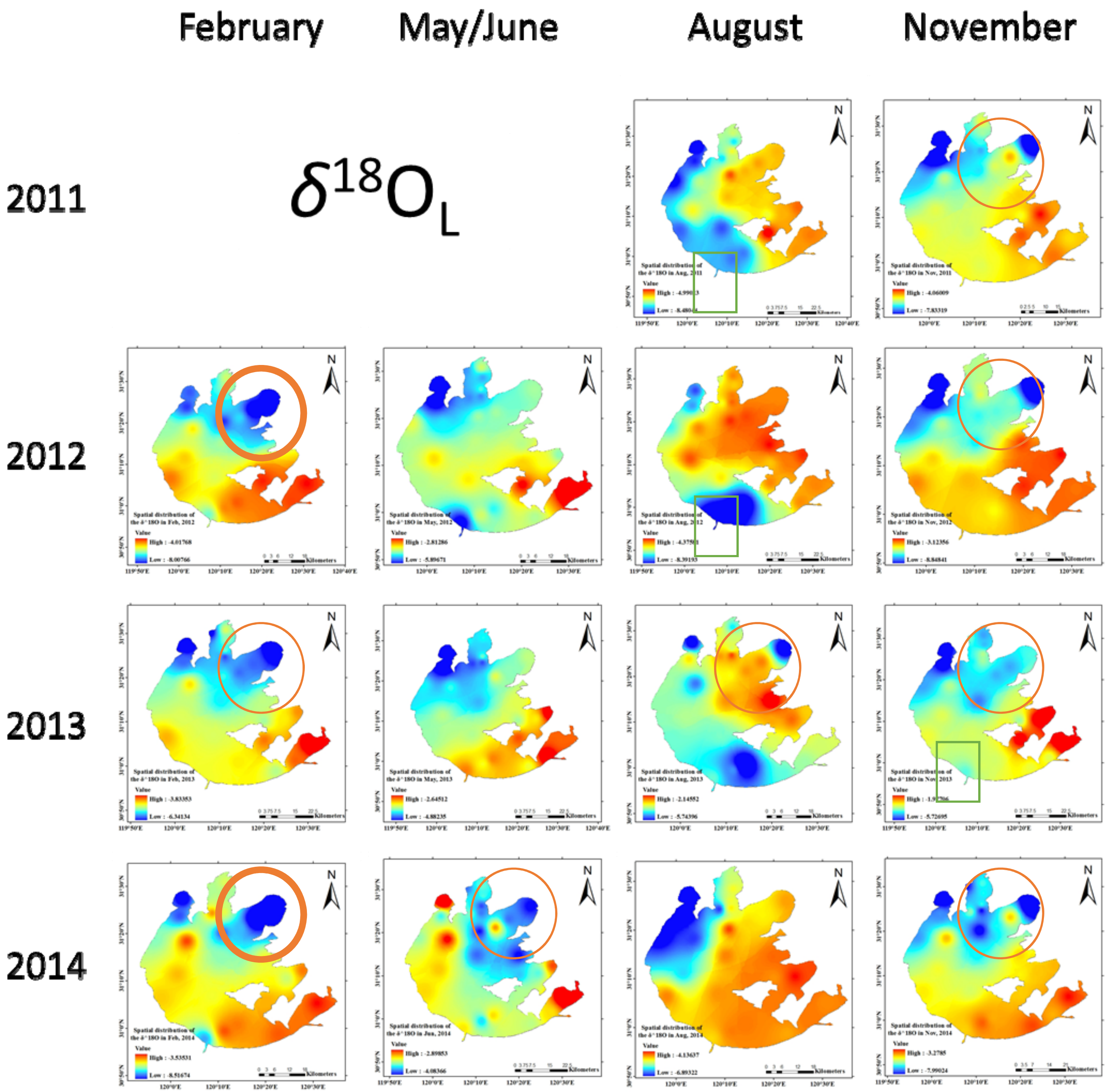
Outflow region: higher δD_L and $\delta^{18}O_L$, lower d_L

water in the outflow region: stayed in the lake, underwent more evaporation, so *d* became lower.

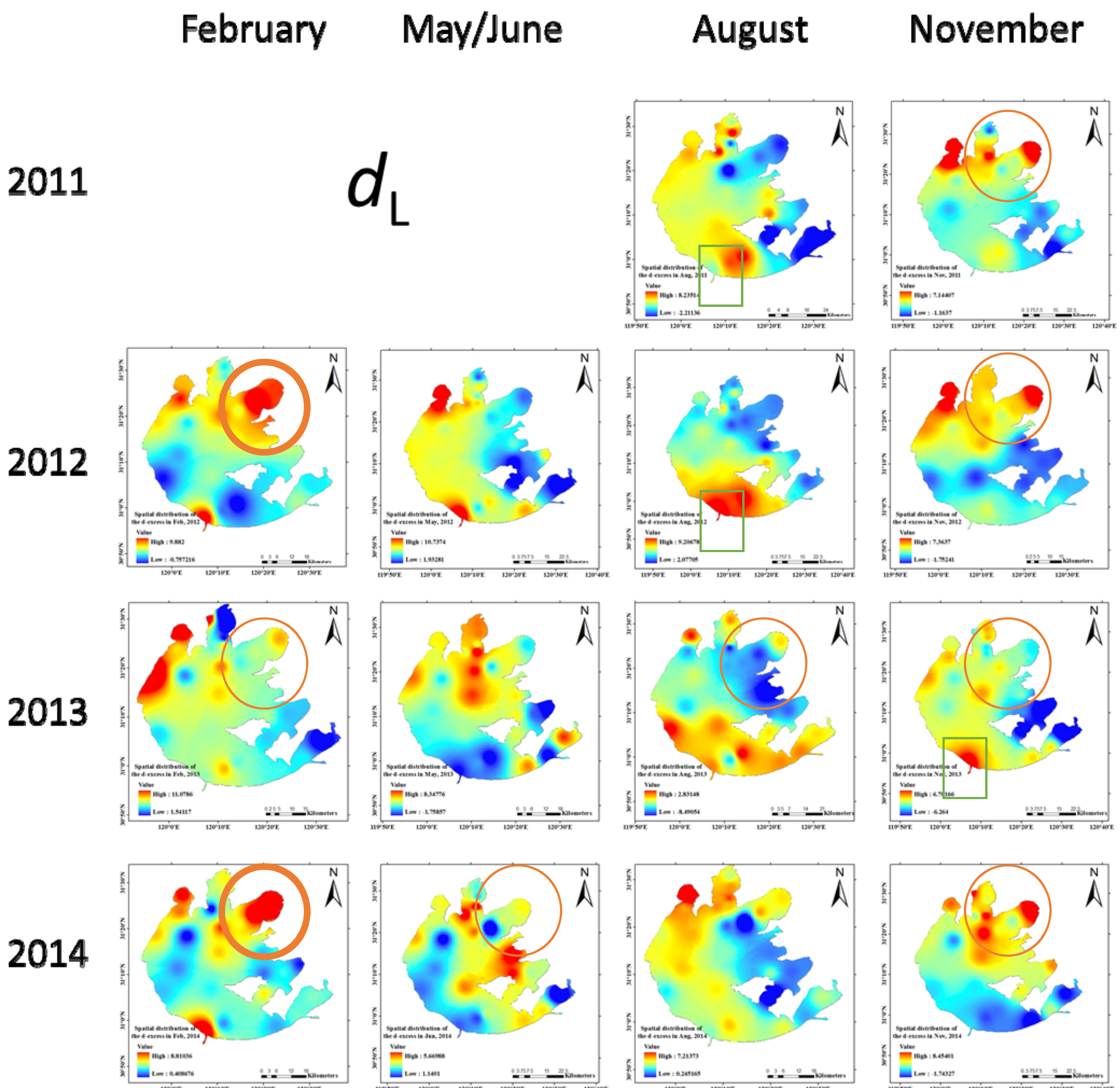
Note: Mean value of 12 seasonal lake surveys (Aug 2011 to Jun 2014)



Note: circle – inflow from Wangyu river; square – inflow from Hangjia lake region

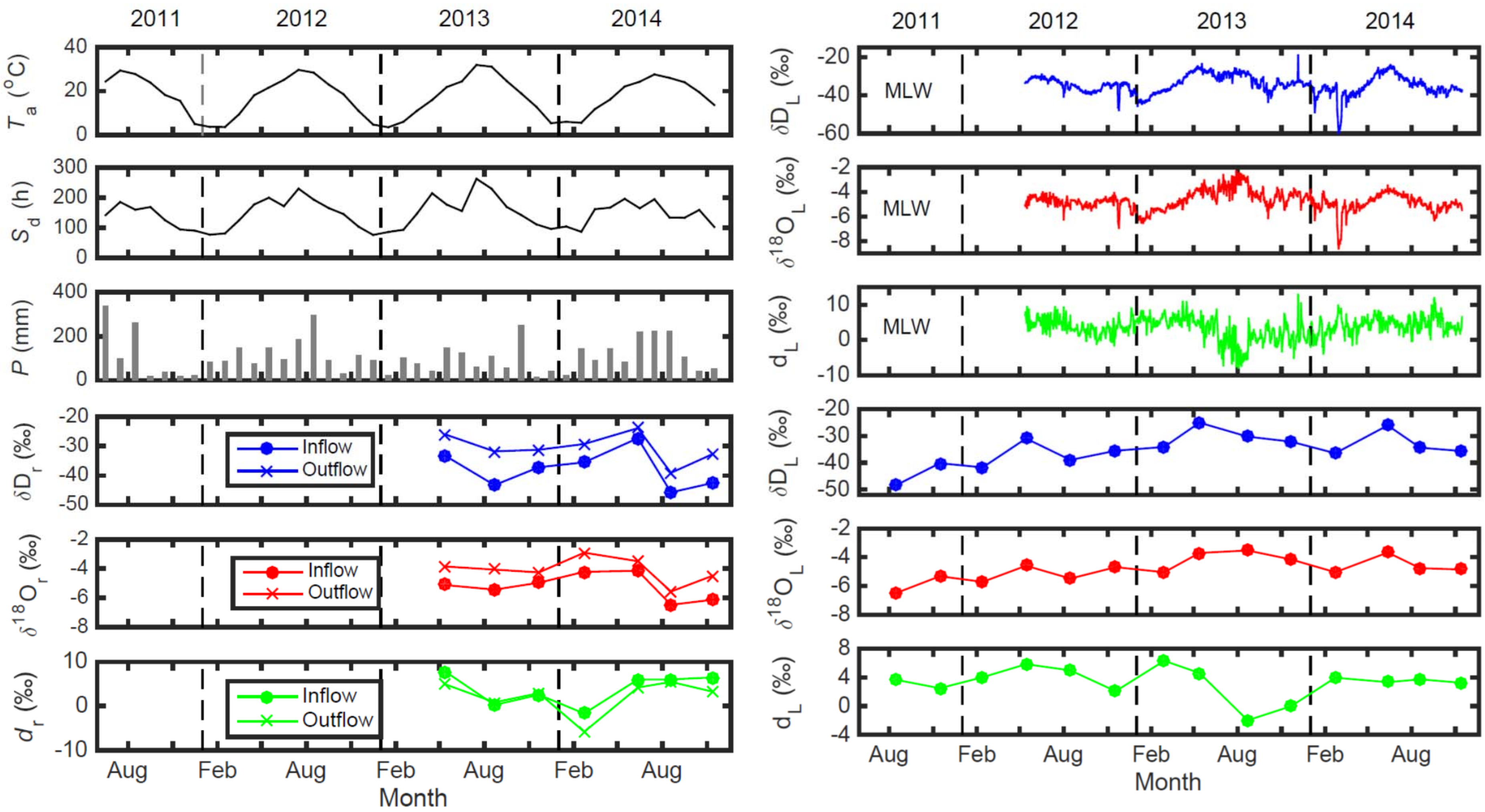


Note: circle – inflow from Wangyu river; square – inflow from Hangjia lake region

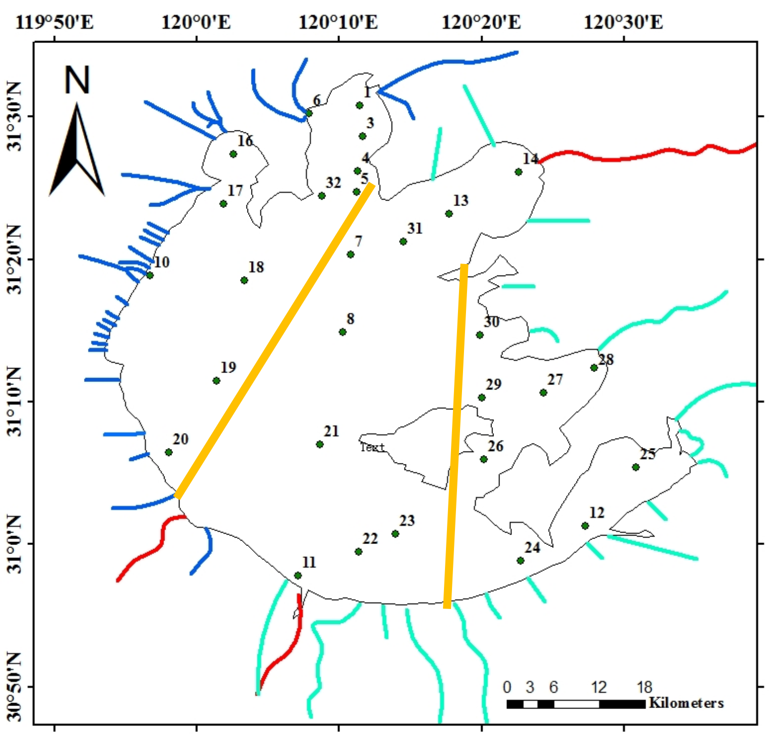


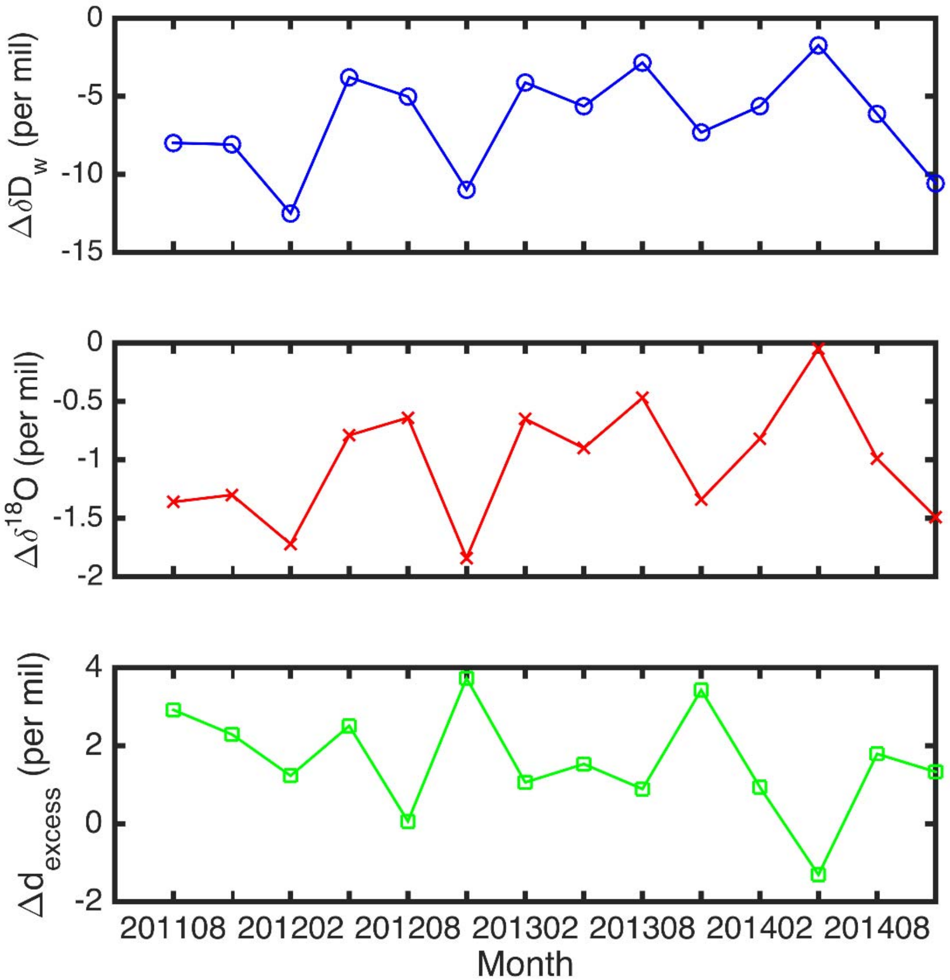
Note: circle – inflow from Wangyu river; square – inflow from Hangjia lake region

Seasonality of meteorological variables, lake and river water isotopes



Difference of lake water isotope between inflow and outflow regions



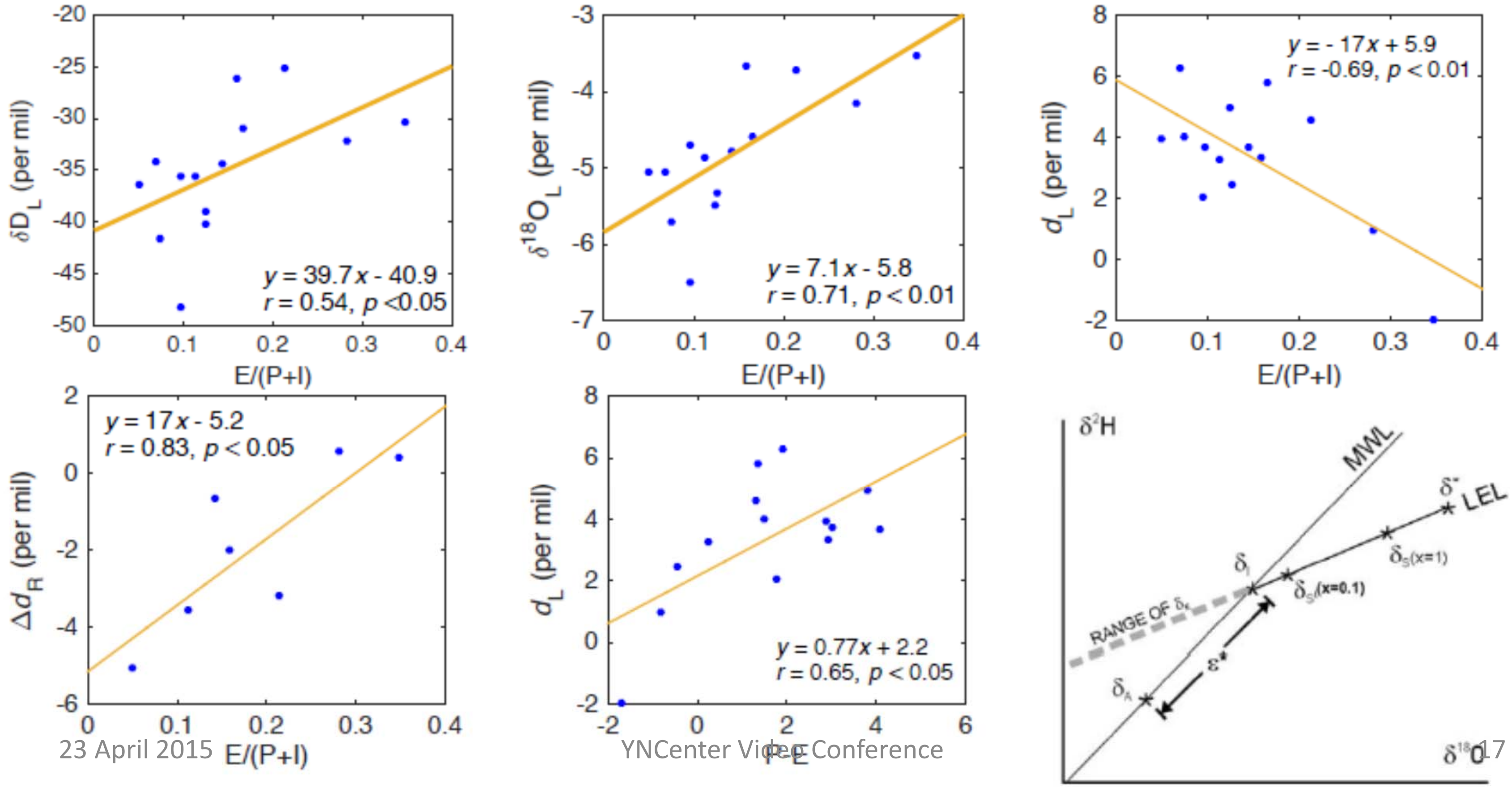


- The Gradients of δD and δ^{18}O were low in warm seasons and high in cold seasons.
- d-excess gradient is high in cold season is high low in warm season.

Lake and river water isotope versus P-E, E/(P+I), and depth

	whole-lake water			lake outflow region - inflow region			river outflow-inflow		
r	δD_L	$\delta^{18}O_L$	d_L	$\Delta\delta D_L$	$\Delta\delta^{18}O_L$	Δd_L	$\Delta\delta D_R$	$\Delta\delta^{18}O_R$	Δd_R
P-E	-0.32	-0.50	0.65*	-0.08	-0.15	0.25	-0.69	-0.27	-0.54
E/(P+I)	0.54*	0.71**	-0.69**	-0.40	-0.30	-0.05	0.33	-0.21	0.83*
depth	-0.40	-0.42	0.16	0.02	0.06	-0.12	-0.22	-0.47	0.48

x = E/(P+I) throughflow index, i.e. the fraction of total water inputs lost by evaporation.



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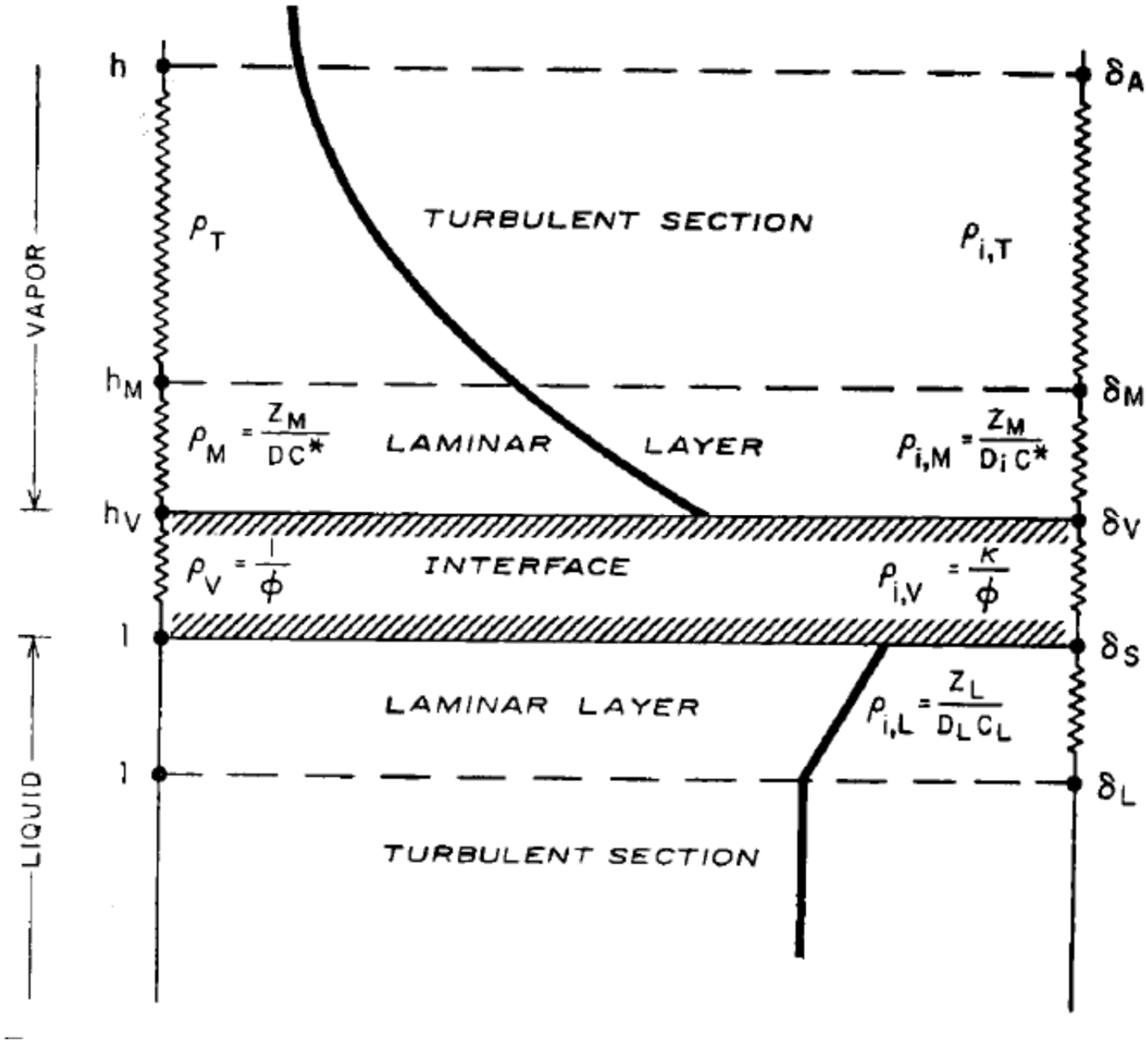
A laminar layer model for an isolated liquid



Turbulent or eddy diffusion

Molecular diffusion

Kinetic fractionation

Equilibrium fractionation

Molecular diffusion

Turbulent or eddy diffusion

(Craig & Gorden, 1965)

Equilibrium fractionation effect

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

$$\alpha_{\mathrm{eq}} = \left(\frac{R_{liquid}}{R_{vapor}}\right)_{eqlb} = \frac{p_{H2O}{}^{16}}{p_i} = 1 + \varepsilon_{eq}$$

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

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

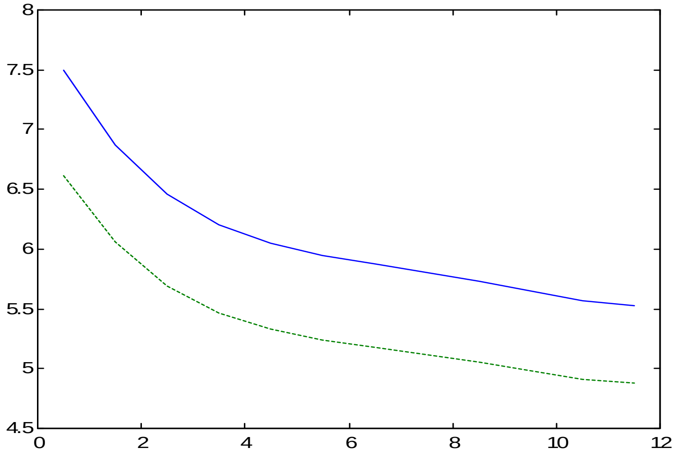
$$\alpha_{\mathrm{eq,D}} = \exp\left(\frac{24.844 \times 10^3}{T_s^2} - \frac{76.248}{T_s} + 52.612 \times 10^{-3}\right)$$

(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 (1979) 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)

Craig-Gordon model:

$$\delta_{\mathrm{E}} = \frac{\alpha_{\mathrm{eq}}\delta_{\mathrm{L}} - h\delta_{\mathrm{a}} - \varepsilon_{\mathrm{eq}} - (1-h)\varepsilon_{\mathrm{k}}}{(1-h) + (1-h)\varepsilon_{\mathrm{k}} \times 10^{-3}}$$

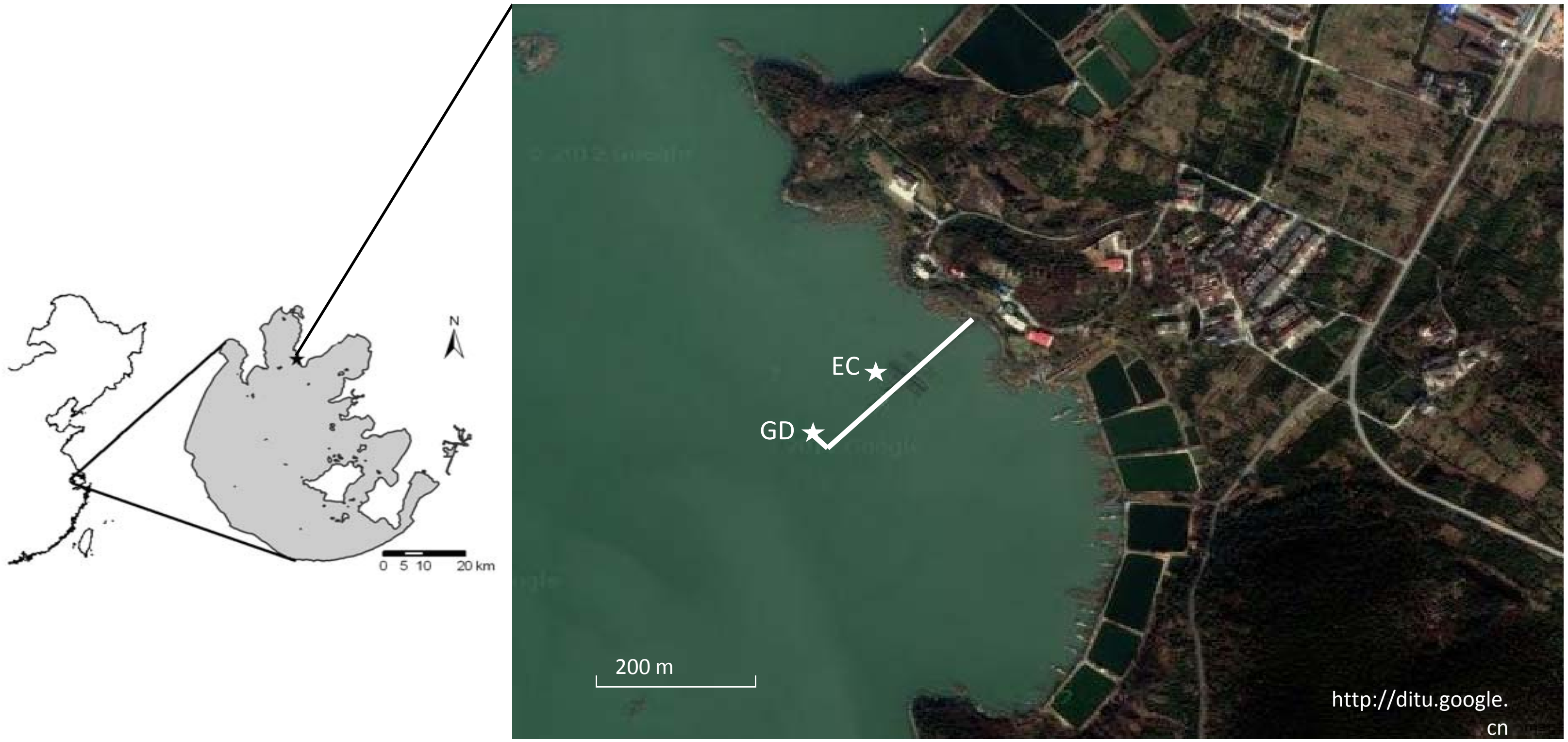
δ_E: isotopic composition of evaporation
δ_L: isotopic composition of lake water
δ_a: isotopic composition of atmospheric vapour

h: relative humidity reference to water surface temperature

ε_k: kinetic fractionation factor
ε_{eq}, α_{eq}: equilibrium fractionation factors

(Craig & Gordon, 1965)

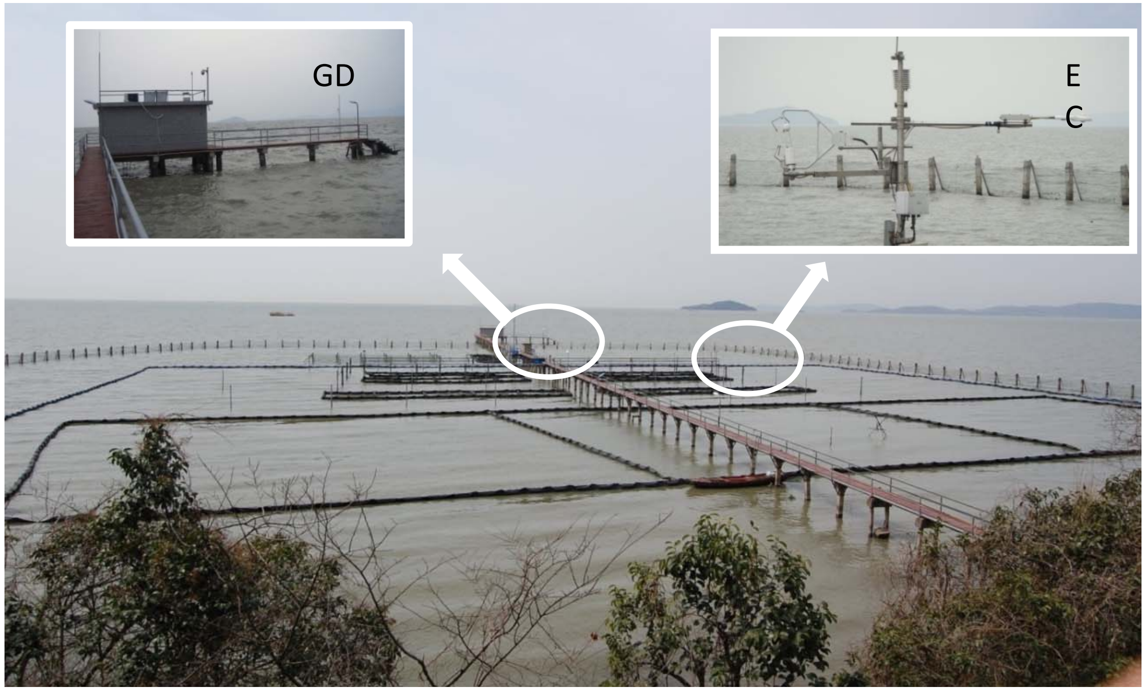
In-situ measurement of isotopic water vapor and evaporation



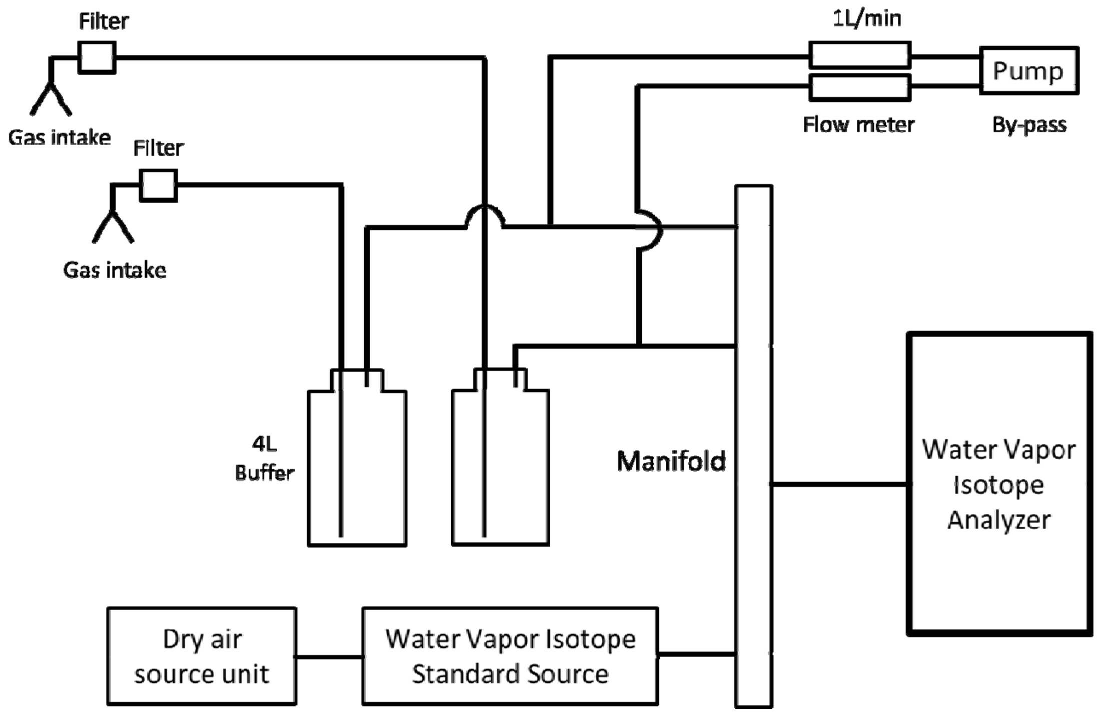
The experiment site (31°24′N, 120°13′E) was in the north part of Lake Taihu, which is the third largest freshwater lake in China, with a water surface area of 2400 km^2 and a mean water depth of 1.9 m

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.



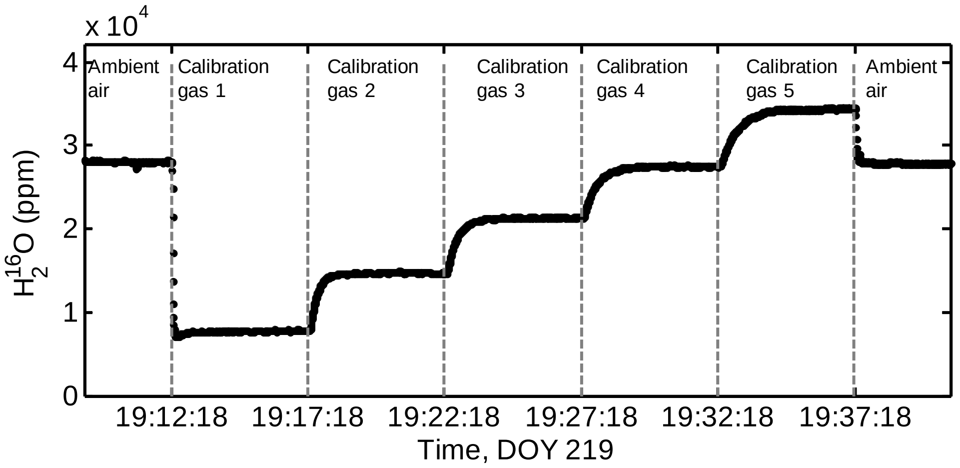
Schematic Design Diagram



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.

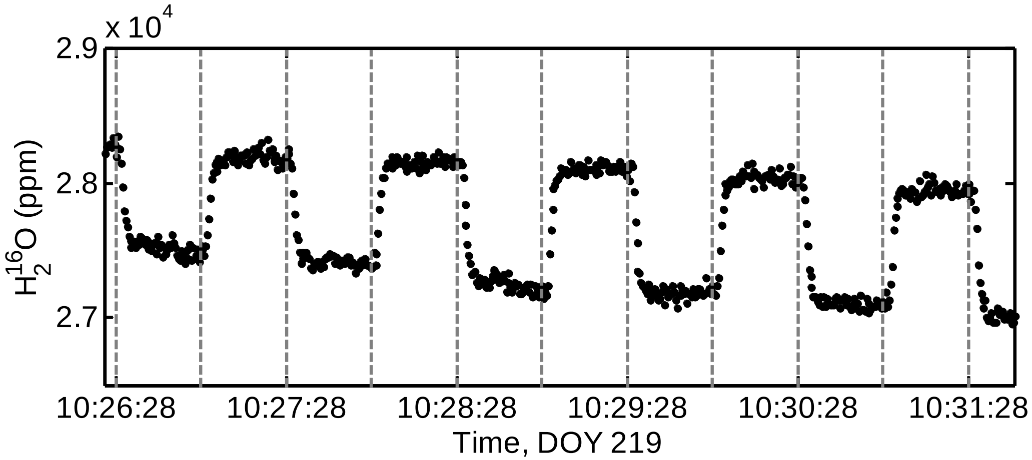
Instrument Performance (1/2)

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:



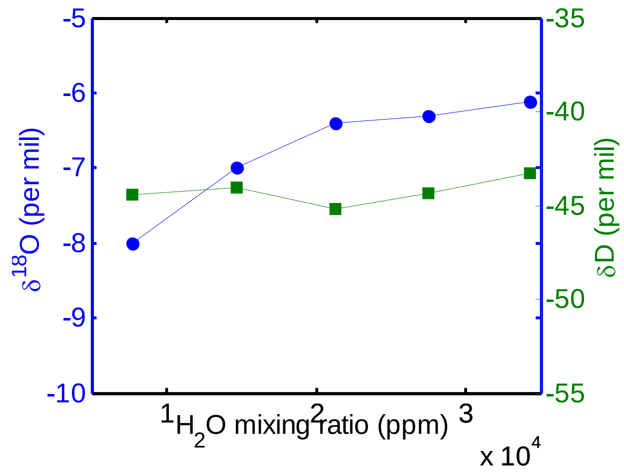
When measuring the ambient air, the manifold switched between the two intakes every 30 s.

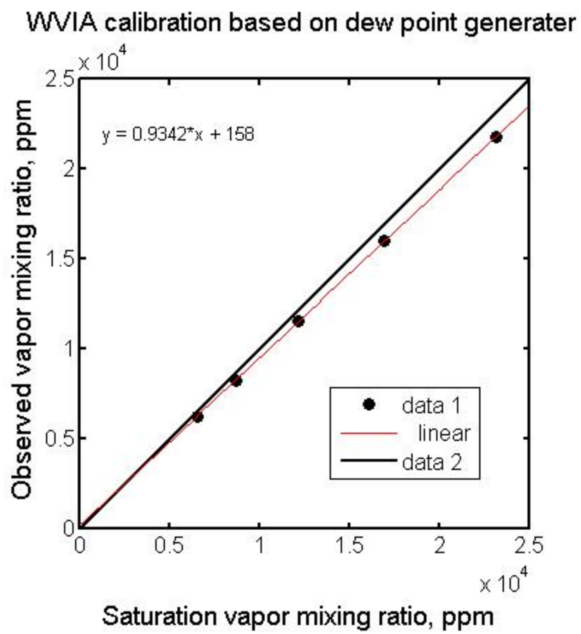
The measurement approached steady state in less than 10 s after each switching.

Instrument Performance (2/2)

Non-linearity & calibration

The analyzer displayed nonlinear behavior. The measured $\delta^{18}O$ 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.





Calibration methods

Step 1: calibrate the ambient air using calibration gas 1 & 2

$$R_1 = R_c \cdot \frac{x_{s,1}}{x'_{s,1}} \cdot \frac{x'_a}{x_a} \qquad \delta_1 = \left(R_1 / R_{VSMOW} - 1\right) \times 1000$$

$$R_2 = R_c \cdot \frac{x_{s,2}}{x'_{s,2}} \cdot \frac{x'_a}{x_a} \qquad \delta_2 = \left(R_2 / R_{VSMOW} - 1\right) \times 1000$$

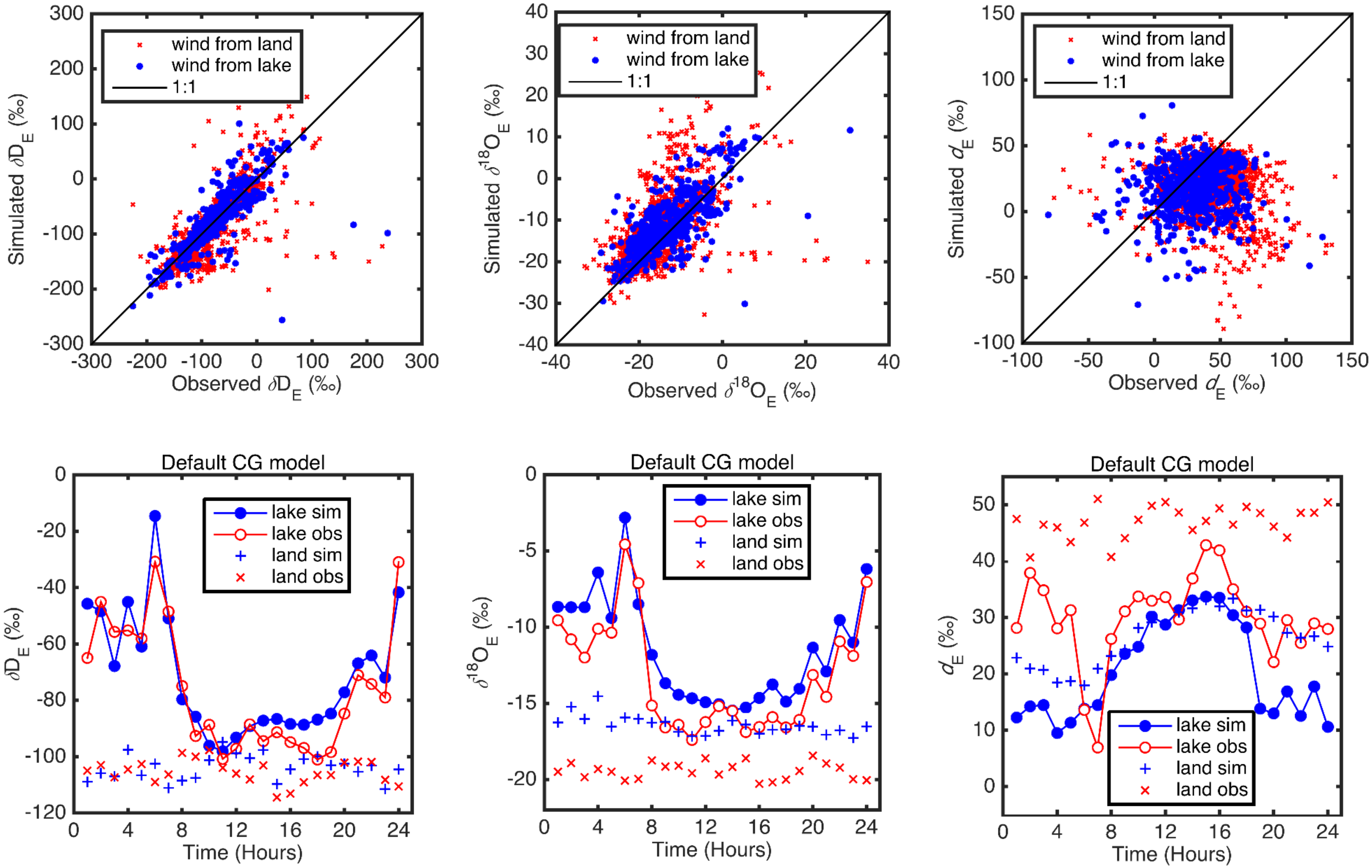
Step 2: calculate the isotopic value of ambient water vapor

$$\delta_v = \delta_1 + \frac{\delta_2 - \delta_1}{x_{s,2} - x_{s,1}} \left(x_a - x_{s,1}\right)$$

Step 3: calculate the isotopic value of evaporation

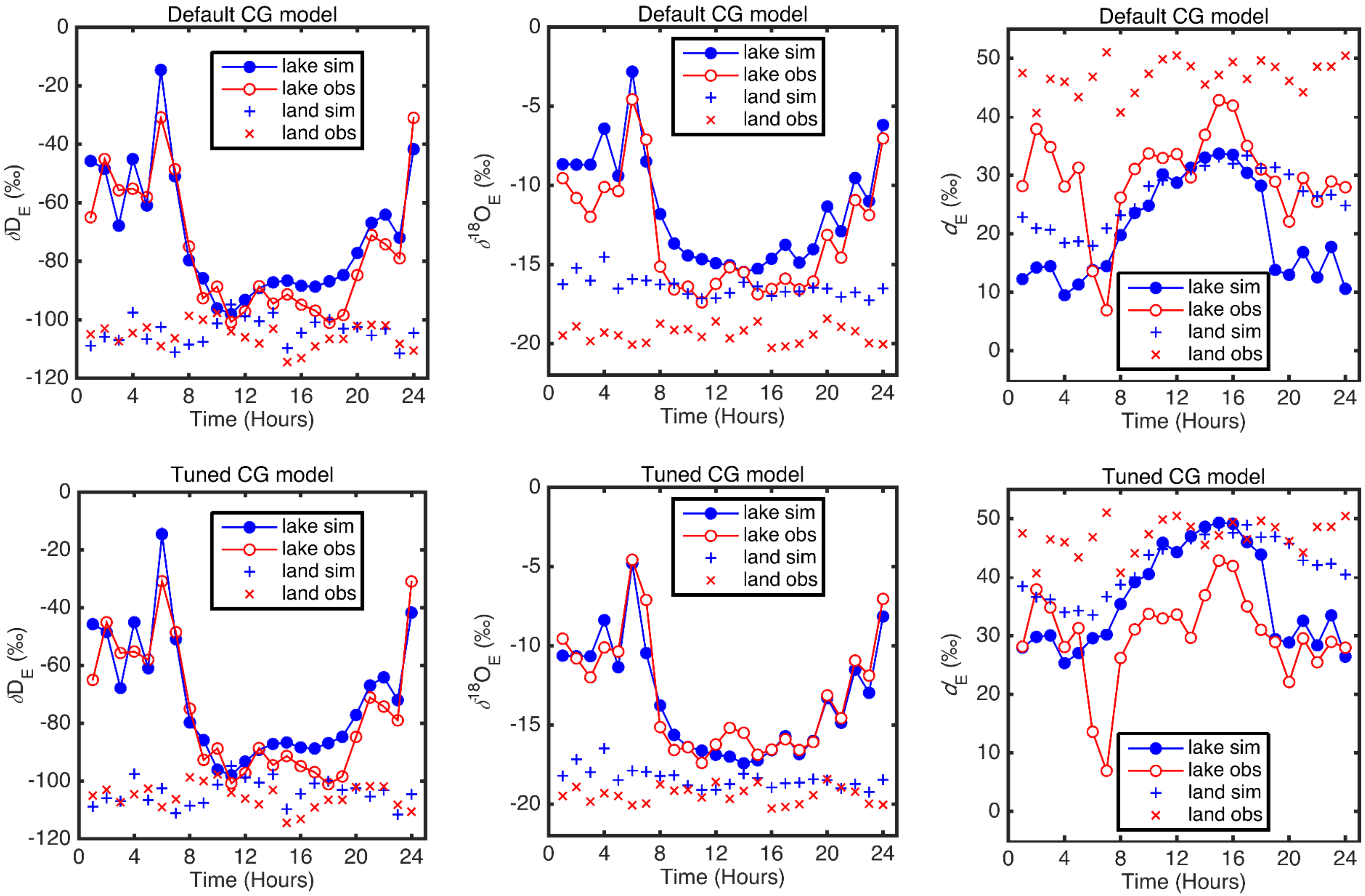
$$R_E = R_c \cdot \frac{x_{s,2} - x_{s,1}}{x'_{s,2} - x'_{s,1}} \cdot \frac{x'_{a,2} - x'_{a,1}}{x_{a,2} - x_{a,1}}$$

Validation of CG model



Note: continuous days, DOY 225-233, 482-530, 1000-1020

Sensitivity analysis on kinetic fractionation factors



Tuned CG model: $\varepsilon_k{}^{18}O$ + 2 ‰, $\varepsilon_k D$ default.

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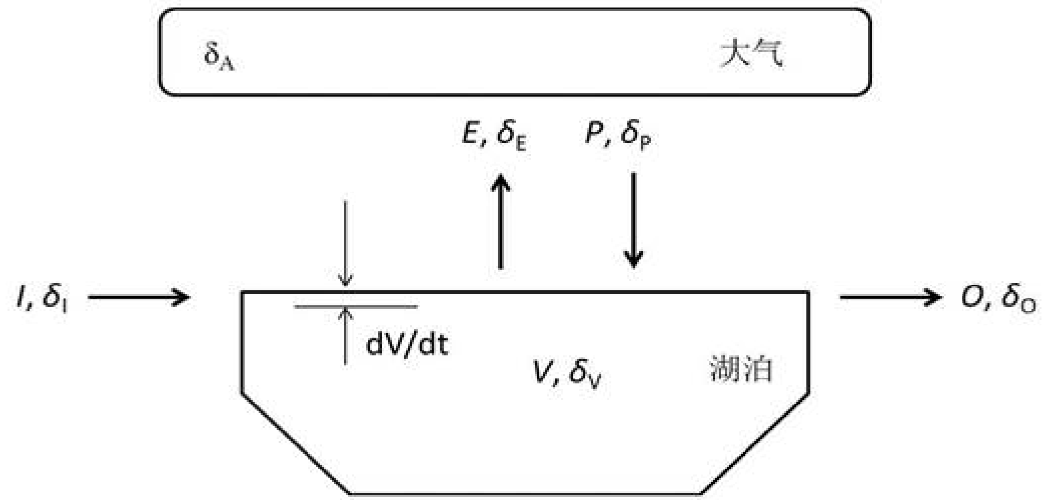
Isotopic mass balance equation



水分平衡方程为:

$$I + P = E + dV + O \tag{6}$$

同位素质量守恒方程为:

$$\delta_I I + \delta_P P = \delta_E E + \delta_V \mathrm{d}V + \delta_O O \tag{7}$$

湖泊蒸发的同位素含量计算公式为:

$$\delta_E = (\delta_I I + \delta_P P - \delta_V dV - \delta_O O) / E \tag{8}$$

Isotopic mass balance method

Month	Water budgets (× 10^8 m^3)						δD (per mil)					$δ^{18}O$ (per mil)				
	S	$ΔS$	P	I	O	E	$Δ(Sδ_S)$	$δD_P$	$δD_I$	$δD_O$	$δD_E$	$Δ(Sδ_S)$	$δD_P$	$δD_I$	$δD_O$	$δD_E$
201305	47.0	3.3	3.6	7.0	5.0	2.3	-72.4	-42.0	-36.7	-28.0	-86.2	12.7	-6.4	-5.2	-4.0	-23.1
201306	51.3	5.4	3.0	10.6	6.2	2.0	-142.2	-62.6	-39.7	-29.7	-138.9	-96.2	-8.7	-5.3	-4.0	19.0
201307	51.5	-5.1	1.4	8.5	11.1	3.9	148.1	-43.8	-42.5	-31.4	-57.0	-61.3	-6.6	-5.4	-4.1	13.3
201308	48.4	-0.9	2.6	9.9	9.1	4.3	25.7	-51.5	-41.6	-31.6	-65.6	-58.2	-7.5	-5.3	-4.2	5.5
201309	48.3	0.7	1.4	9.6	7.7	2.6	-32.3	-47.0	-39.5	-31.4	-65.7	-31.8	-6.9	-5.2	-4.2	2.0
201310	52.3	7.7	6.0	14.1	10.8	1.7	-254.4	-32.2	-37.6	-31.2	-80.8	-63.0	-5.3	-5.0	-4.3	3.9
201311	51.8	-8.6	0.3	3.8	11.5	1.2	264.0	-26.8	-36.7	-30.7	-49.5	-7.3	-4.6	-4.8	-3.9	28.5
201312	46.1	-2.3	1.0	5.7	8.4	0.5	63.5	-19.8	-36.2	-30.0	-69.1	-53.6	-3.9	-4.5	-3.4	109.0
201401	43.6	-2.6	0.6	6.1	9.1	0.2	77.9	-21.0	-35.6	-29.4	-185.9	-48.1	-4.0	-4.3	-3.0	217.4
201402	46.0	7.2	3.5	8.4	4.1	0.6	-265.5	-37.2	-33.8	-28.2	-54.9	-54.7	-5.8	-4.2	-3.0	19.8
201403	49.3	-0.7	2.2	8.0	10.0	0.9	42.8	-23.0	-31.5	-26.7	-88.5	143.1	-4.2	-4.2	-3.2	-174.3
201404	50.6	3.5	3.5	8.1	6.5	1.6	-89.8	-35.3	-29.2	-25.2	-64.8	123.6	-5.6	-4.2	-3.4	-94.3
201405	50.1	-4.4	2.0	6.2	10.4	2.2	145.2	-37.3	-29.2	-25.4	-61.8	160.0	-5.8	-4.4	-3.7	-73.7
201406	50.9	5.9	5.3	9.5	6.5	2.3	-167.3	-61.2	-36.8	-31.7	-127.0	-81.4	-8.6	-5.4	-4.6	6.4
201407	57.2	7.0	5.3	14.6	10.4	2.6	-239.8	-57.6	-44.3	-37.8	-125.4	-239.4	-8.2	-6.3	-5.4	62.3
201408	61.3	1.2	5.3	10.8	12.6	2.3	-58.0	-67.9	-44.7	-37.0	-138.1	-150.6	-9.3	-6.4	-5.2	42.6
201409	59.7	-4.4	2.5	9.5	14.4	2.1	151.8	-61.3	-43.5	-34.7	-107.5	-3.1	-8.6	-6.2	-4.8	-3.9
201410	54.2	-6.5	1.0	4.9	10.5	1.9	227.8	-28.8	-42.8	-33.1	-62.1	8.8	-4.9	-6.1	-4.6	2.4
201411	50.7	-0.5	1.3	7.9	8.7	1.0	16.0	-37.9	-41.8	-32.9	-108.2	-5.6	-5.9	-6.0	-4.5	-10.7

Data source:

S, $ΔS$, I: Taihu bureau

P: mean precipitation of Wuxi, Dongshan and Huzhou meteorological station

E: Priestly-Taylor equation based on the MLW observation

O: calculated using water mass balance equation

$Δ(Sδ_S)$: $Δ(Sδ_S) = ΔS*δ_S + S*Δδ_S$, first interpolate seasonal lake water isotope to daily value, then calculate monthly average $δ_S$ and $Δδ_S$ (month end – month begin) based on the daily data.

$δD_P$, $δ^{18}O_P$: calculated from monthly mean air temperature and month total sunshine duration using the regression equation of Liu et al. (2014), calculated $δD_P$ for Wuxi, Dongshan and Huzhou respectively, then got mean value.

$δD_I$, $δD_O$, $δ^{18}O_I$, $δ^{18}O_O$: interpolated to daily value from seasonal lake survey, then calculate month mean using daily data.

$δD_E$, $δ^{18}O_E$: calculated using isotopic mass balance equation.

Isotopic mass balance method vs Craig-Gorden model

Results of May 2013

Isotopic mass balance method

δD_E = -86.2 ‰

$\delta^{18}O_E$ = -23.1 ‰

Flux weighted isotope based on tuned CG model

δD_E = -86.7 ‰

$\delta^{18}O_E$ = -15.8 ‰

Sensitivity analysis on precipitation isotope

$\delta^{18}O_P$ = -1.8 ‰

Thanks for your attention!

http://yncenter.sites.yale.edu