Validation of the Craig-Gordon isotopic model for lake evaporation

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Outlines

1. Introduction
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1. Introduction

- The theory on isotopic composition of evaporation ($\delta_E$) 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 $\delta_E$ 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:

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

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

\[
\delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000, \%_{\circ}
\]
Scientific hypothesis

Well-mixed assumption:
\[ \delta_{L,e} = \delta_{L,b} \]

In-situ measurement
\[ \delta_{E,\text{sim}} = \delta_{E,\text{obs}} : \text{well mixed} \]
\[ \delta_{E,\text{sim}} \neq \delta_{E,\text{obs}} : \text{not well mixed} \]

C-G simulation

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2. Model

Craig-Gordon model:

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

- $\delta_E$: isotopic composition of evaporation
- $\delta_L$: isotopic composition of lake water
- $\delta_a$: isotopic composition of atmospheric vapour
- $h$: relative humidity reference to water surface temperature
- $\varepsilon_k$: kinetic fractionation factor
- $\varepsilon_{eq}$, $\alpha_{eq}$: equilibrium fractionation factors
Equilibrium fractionation effect:

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

\[
\alpha_{eq} = \left( \frac{R_{\text{liquid}}}{R_{\text{vapor}}} \right)_{eq} = \frac{p_{\text{H}_2\text{O}}^{16}}{p_i} = 1 + \varepsilon_{eq}
\]

\(p_i\): 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 $\varepsilon_k$ 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. OBSERVATION

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

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 km² 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 $\text{H}_2^{16}\text{O}$, HDO and $\text{H}_2^{18}\text{O}$ 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)

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.

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 $\delta^{18}$O and $\delta$D 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

Doy 217: Start
Doy 229: copy data
Doy 235: site visit

Aug 4

$4 \times 10^4$

$H_2^{16}O$ mixing ratio, ppm

Calibration
Ambient air

Doy 220-222: Move the instrument & reconnet
Doy 233: power outage
Doy 252: power outage
Circuit board in the analyzer was burned down

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Doy 292: change water,
Doy 322: change new microdrop generator
Big bias from GMWL
Doy 354: restart, change pump
Change water

Doy 252-:
Calibration unit stop working

Microdrop generator blocked

Doy 329:
Change water
Dry air unit got dirty, clean it.

Doy 334:
Power outage

Doy 335-360:
fixed dry air unit

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Jan 1-20, 2013

Doy 15:
Change water, pump and filter.
No flow for outside pump stopping working
Filter of intakes were dirty, but did not changed them

Doy 385.5-387.7: no data
Jan 21 - Feb 28, 2012

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Filters were dirty, changed on DOY 396

Doy410: restarted

Doy423: restarted; Change water

Stop working

$H_2^{16}O$ mixing ratio, ppm

$10^4$
March 1 – 31, 2013

Doy 441:  Change water (small bottle), Change filters

Doy 445-450: power outage

Doy 450: power on, wrong absorption peak
April 1-17, 2013

Microdrop generator blocked

Graph showing $H_2^16O$ mixing ratio, ppm vs DOY from April 1-17, 2013.
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. VALIDATION OF CG MODEL

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

![Graphs showing fractionation factors for H218O and HD0 over DOY of 2012.](image)
4.3 δ value of evaporation (1/2)
4.3 $\delta$ value of evaporation (2/2)
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