Postprint: Simulation of Stable Hydrogen and Oxygen Isotopes in Atmospheric Water Vapor Based on Evaporation Pan Experiments

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Abstract

Atmospheric water vapor hydrogen and oxygen stable isotopes directly reflect key information regarding processes such as transport, mixing, and phase change of water in the atmosphere. While evaporation pan experiments can simulate the composition of atmospheric water vapor hydrogen and oxygen stable isotopes, the reliability of such simulation methods still requires validation with observational data. An evaporation pan experiment was conducted in Lanzhou, Gansu Province from September to November 2019 to simulate daily atmospheric water vapor hydrogen and oxygen stable isotopes; concurrently, an online atmospheric water vapor hydrogen-oxygen stable isotope analyzer was employed for real-time monitoring to validate the reliability of the simulation results. The study found: (1) The \$ \$18O in atmospheric water vapor simulated using the Craig-Gordon linear resistance model under natural evaporation conditions and the water body isotope mass balance method exhibited good consistency with directly measured \$ \$18O in atmospheric water vapor, with a root mean square error of 4.5‰, a mean absolute error of 3.2‰, and a mean bias of 0.03‰. (2) The simulation residuals of \$ \$18O in atmospheric water vapor showed certain correlations with relative humidity (R2=0.43), evaporation residual ratio (R2=0.39), and residual water body isotope values (R2=0.39). (3) The model demonstrated high sensitivity to relative humidity, with model errors increasing under low relative humidity conditions. During the late experimental period, when the evaporation residual ratio was low and the residual water body isotopes were enriched, the water vapor isotope simulation residuals were larger compared to those in the early experimental period.

Full Text

Simulation of Stable Hydrogen and Oxygen Isotopes in Atmospheric Water Vapor Based on an Evaporation Pan Experiment

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Abstract: The stable hydrogen and oxygen isotopes in atmospheric water vapor directly reflect key information about water transport, mixing, and phase-change processes in the atmosphere. While evaporation pan experiments can simulate the isotopic composition of atmospheric water vapor, the reliability of such simulation methods requires validation against measured data. This study conducted an evaporation pan experiment in Lanzhou from September to November 2019 to simulate daily stable hydrogen and oxygen isotopes in atmospheric water vapor. Simultaneous real-time monitoring was performed using an online atmospheric water vapor isotope analyzer to validate the simulation results. The study found that: (1) The simulated δ^{18}O in atmospheric water vapor showed good consistency with directly measured values, with a root mean square error of 4.5‰, a mean absolute error of 3.2‰, and a mean bias error of 0.03‰. (2) The simulation residuals were correlated with relative humidity ($R^2 = 0.43$), remaining water ratio ($R^2 = 0.39$), and the isotopic values of the remaining water ($R^2 = 0.39$). (3) The Craig-Gordon model exhibited high sensitivity to relative humidity, with model errors increasing under low humidity conditions. Under conditions of low remaining water ratio and isotopically enriched remaining water at the experimental end stage, the water vapor isotope simulation residuals were substantially larger than those in the early experimental stage.

Keywords: stable hydrogen and oxygen isotopes; evaporation pan; simulation; atmospheric water vapor

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Introduction

Stable hydrogen and oxygen isotopes (δ^2H and δ^{18}O) in water bodies serve as natural tracers for studying hydrological cycles and reconstructing paleoclimate information. Early research on atmospheric water vapor isotopes primarily relied on the low-temperature cold trap method, which obtains liquid water samples by cryogenic condensation of air. This method demands rigorous experimental operation and often fails to characterize fine-scale temporal and spatial variations in atmospheric vapor isotopes, particularly when water vapor content is low, as liquefaction becomes time-consuming. With advancements in laser spectroscopy technology, real-time online monitoring of stable hydrogen and oxygen isotopes in atmospheric water vapor has become feasible. Laser spectroscopy overcomes the limitations of cold trap methods for continuous measurements, though relatively high costs prevent widespread deployment.

Atmospheric water vapor constitutes the necessary material condition for precipitation formation, and its stable isotopes correspondingly contain environmental information about evaporation, transport, and condensation processes. Compared to precipitation, atmospheric vapor isotopes provide direct evidence for diagnosing atmospheric water processes, with advantages in temporal and spatial continuity. Vapor isotopes enable all-weather continuous monitoring, unlike precipitation isotopes that only represent conditions during precipitation events. Combined with airships, unmanned aerial vehicles, and satellite remote sensing, vapor isotopes can achieve three-dimensional spatial coverage, whereas ground precipitation isotopes have limitations in characterizing vertical atmospheric processes. Furthermore, raindrops may undergo sub-cloud secondary evaporation during descent through unsaturated air, affecting the spatiotemporal characteristics of precipitation isotopes, while vapor isotope monitoring can mitigate this information distortion.

When direct monitoring of atmospheric vapor isotopes is unavailable, the Craig-Gordon linear resistance model and water isotopic mass balance method can be employed for simulation, with results validated against measured vapor isotope data. To investigate the reliability of these methods for calculating atmospheric water vapor isotopes in arid and semi-arid regions, this study designed an evaporation pan experiment to simulate stable hydrogen and oxygen isotopes in atmospheric water vapor in Lanzhou, Gansu Province. By combining synchronous monitoring records from an online water vapor isotope analyzer, we evaluated the reliability of the evaporation pan simulation results, aiming to provide a relatively simple method for obtaining continuous atmospheric water vapor isotope data.

1. Materials and Methods

1.1 Evaporation Pan Experiment

The experiment was conducted at the new campus of Northwest Normal University in Lanzhou, Gansu (36°6 N, 103°44 E), located in a monsoon marginal zone with a semi-arid climate characterized by large annual temperature ranges and summer-concentrated precipitation. The evaporation pan experiment ran from September 1 to November 30, 2019, with an average temperature of 14.4°C and average relative humidity of 62%.

A rectangular transparent glass tank (420 mm × 220 mm × 200 mm) served as the evaporation pan, placed in an open, well-ventilated area. During rainfall events, a transparent plastic film cover was placed 0.5 m above the pan to prevent precipitation from entering, and promptly removed after rainfall ceased. The experiment began by filling the pan with local tap water. Daily water level measurements were recorded at the same time each day using a steel ruler. After thoroughly mixing the water, 30 mL samples were extracted with a syringe and stored in sealed glass bottles under refrigeration. To minimize water loss effects from sampling, a supplementary tank of identical size and material was placed 0.5 m away, filled with the same initial water volume and allowed to evaporate simultaneously. Daily 30 mL water samples from this supplementary tank were used to replenish the main evaporation pan.

Atmospheric temperature and relative humidity were monitored and recorded continuously throughout the experiment. The extracted daily remaining water samples were analyzed for stable hydrogen and oxygen isotopes using a Los Gatos Research LWIA-45-EP liquid water isotope analyzer, with measurement errors less than 0.5‰ for δ^{18}O and 2‰ for δ^{2}H.

Isotopic ratios are expressed as per mil (‰) deviations relative to Vienna Standard Mean Ocean Water (VSMOW):

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

where R_{sample} represents the isotopic ratio of the evaporating water sample and R_{VSMOW} represents the isotopic ratio of VSMOW.

1.2 Atmospheric Water Vapor Isotope Measurements

Atmospheric water vapor isotopes were measured using a Los Gatos Research Ultraportable Water Vapor Isotope Analyzer (UWVIA-915) concurrently with the evaporation pan experiment. Based on off-axis integrated cavity output spectroscopy, this instrument calculates concentrations from absorption intensities of specific infrared wavelengths by different isotopologues, achieving sampling frequencies up to the second level with measurement precision of \$±\$0.05‰.

The instrument employs a Water Vapor Isotope Standard Source (WVISS) system to generate standard vapor. During measurement, data from the first and last minutes of each concentration gradient were discarded, using only stable isotopic values from the middle portion of each gradient as the standard vapor isotopic value to minimize memory effects. When measuring atmospheric vapor isotopes, the first 10 minutes of data were discarded, with measurements commencing only after atmospheric vapor concentrations stabilized. Concentration effect calibration followed the method of [?], where the isotopic composition of standard water was measured using the LWIA-45-EP liquid water isotope analyzer and used as the true value for standard vapor. The difference between this true value and the analyzer-measured standard vapor isotope value was used to fit a quadratic curve against vapor concentration, yielding measurement error values for concentration effect calibration.

1.3 Simulation Calculations Based on Evaporation Pan Experiments

The Craig-Gordon linear resistance model is widely applied for estimating evaporative vapor isotopes:

$$\delta_E = \frac{\delta_L - h\delta_A - \varepsilon^*}{1 - h + \varepsilon_K/1000}$$

where δ_E represents the isotopic ratio of evaporating vapor, δ_A represents atmospheric vapor isotopic ratio, δ_L represents remaining water isotopic ratio, h is relative humidity, α^* is the equilibrium fractionation coefficient obtainable from [**?**], and ε_K is the kinetic fractionation factor (14.2‰ for oxygen and 12.5‰ for hydrogen).

[**?**] demonstrated that evaporating water isotopic composition depends on atmospheric vapor isotopes. For a well-mixed water body under natural evaporation, the mass balance equation over time interval dt is:

$$\frac{dV}{dt} = I - Q - E$$

where V is water volume, I is inflow, Q is outflow, and E is evaporation.

The isotopic mass balance equation is:

$$\frac{d(V\delta_L)}{dt} = \delta_I I - \delta_Q Q - \delta_E E$$

This represents the general isotopic mass balance equation. In this experiment, the evaporation pan served as a fixed-volume container with no inflow or outflow, where water volume only decreased due to natural evaporation. Defining $f = V/V_0$ as the evaporation index (ratio of current to initial water volume), the equation can be rearranged as:

$$\delta_L = \frac{\delta_0 - \delta_A - \varepsilon^*}{f^{1-h+\varepsilon_K/1000}} + \delta_A + \varepsilon^*$$

As evaporation proceeds, water isotopes approach a fixed value called isotopic "steady state." Rearranging yields the atmospheric vapor isotope calculation formula from evaporation pan experiments:

$$\delta_A = \delta_L - \frac{\delta_0 - \delta_L}{f^{1-h+\varepsilon_K/1000}} + \varepsilon^*$$

Simulation accuracy was evaluated using root mean square error (RMSE), mean absolute error (MAE), and mean bias error (MBE):

$$\text{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\delta_{\text{obs}} - \delta_{\text{sim}})^2}$$

$$\text{MAE} = \frac{1}{n}\sum_{i=1}^{n}|\delta_{\text{obs}} - \delta_{\text{sim}}|$$

$$\text{MBE} = \frac{1}{n}\sum_{i=1}^{n}(\delta_{\text{obs}} - \delta_{\text{sim}})$$

where δ_{obs} represents measured atmospheric vapor isotopic ratios and δ_{sim} represents simulated values.

2. Results and Discussion

2.1 Temporal Variations of Stable Isotopes

The initial isotopic values of the evaporating water were δ^{18}O = -9.53‰ and δ^{2}H = -65.60‰. As water evaporated from the pan, the remaining water became progressively enriched in heavy isotopes, reaching δ^{18}O = -0.53‰ and δ^{2}H = -14.86‰ by the experiment’ s end. This pattern conforms to fundamental isotopic enrichment principles during evaporation. [**?**] reported similar ranges in an Indian evaporation pan experiment (δ^{18}O from -9.5‰ to -1.5‰), though their experimental conditions featured higher average temperature (26.5°C) and relative humidity (75%) than this study.

During the early experimental stage, isotopic changes in remaining water were relatively gradual. In the final stage, reduced water volume made the system more susceptible to meteorological variations, slightly accelerating isotopic enrichment. Simulated evaporative vapor isotopes also showed progressive enrichment, mirroring the pattern in remaining water but remaining consistently lower than remaining water isotopes.

Measured atmospheric vapor δ^{18}O ranged from -16.5‰ to -9.5‰ (mean = -13.86‰), while δ^{2}H ranged from -125‰ to -80‰ (mean = -113.22‰). Simulated atmospheric vapor δ^{18}O ranged from -17.5‰ to -9.5‰ (mean = -14.21‰), and δ^{2}H ranged from -130‰ to -85‰ (mean = -116.53‰). Temporally, simulated atmospheric vapor isotopes showed good consistency with directly measured values, with closer agreement during early experimental stages and larger deviations in the final stage.

[Figure 1: see original paper]

2.2 Comparison of Measured and Simulated Values

The relationship between δ^{18}O and δ^{2}H in remaining water, simulated atmospheric vapor, and measured atmospheric vapor defines the evaporation line ($\delta^{2}H = 3.76\delta^{18}O - 28.54$). The slope of the evaporation line reflects the degree of non-equilibrium fractionation during evaporation, with lower slopes indicating stronger non-equilibrium effects. This experiment' s evaporation line slope (3.76) was significantly lower than the global meteoric water line slope (8), indicating intense non-equilibrium fractionation that substantially reduced the slope compared to global precipitation.

Compared to measured atmospheric vapor isotopes, simulated values were generally lower, plotting below measured values on the δ^{18}O-δ^{2}H diagram. Both measured and simulated atmospheric vapor isotopes clustered near the global meteoric water line, consistent with [?]. However, the experimental site experienced low relative humidity (62%) and strong evaporation (average daily evaporation of 3.3 mm), with both simulated and measured atmospheric water lines exhibiting lower slopes than the global meteoric water line due to intense kinetic effects. The relatively small pan volume compared to natural lakes made the simulated process more susceptible to environmental factors, further reducing the slope.

Overall, simulated and measured atmospheric vapor isotopes showed similar trends during the observation period, with simulated values generally lower than measured values.

2.3 Sensitivity Analysis

Sensitivity was assessed by examining deviations between simulations with altered parameters and baseline simulations. Relative humidity changes significantly impacted results: when relative humidity decreased by one standard deviation, the deviation reached 3.2‰, greater than the 2.8‰ deviation from a one standard deviation increase. Non-equilibrium kinetic fractionation correlates strongly with relative humidity; lower humidity intensifies kinetic effects, driving evaporation further from equilibrium and increasing simulation deviations.

Temperature effects were comparatively smaller, with deviations within 1.5‰ for a one standard deviation temperature change. The evaporation remaining ratio f showed asymmetric sensitivity: f increases produced larger deviations than decreases of the same magnitude. Remaining water isotopic enrichment and depletion effects were relatively symmetric.

[Figure 3: see original paper]

2.4 Reliability Assessment

Simulation residuals (measured minus simulated δ^{18}O) were analyzed against various parameters. Temperature showed weak correlation with residuals (R^2 =

0.08, $P > 0.05$), indicating temperature was not a primary source of simulation error. Relative humidity demonstrated stronger negative correlation ($R^2 = 0.43$, $P < 0.05$), with residual distribution becoming more dispersed when relative humidity fell below 60%.

The remaining ratio f also correlated with residuals ($R^2 = 0.39$, $P < 0.05$). Small f values indicated less remaining water, making the system more susceptible to isotopic exchange between water and atmosphere. In early experimental stages, as remaining water isotopes increased, residuals transitioned from negative to positive values but remained near zero. In later stages, reduced water volume increased environmental sensitivity, making the evaporation process unstable. The maximum residuals occurred when relative humidity was below 60% and remaining water isotopes were relatively enriched.

Water vapor pressure showed correlations similar to relative humidity ($R^2 = 0.53$ for $\delta^{18}O$ residuals), while atmospheric pressure exhibited no significant correlation ($R^2 = 0.001$). For δ^2H residuals, correlations with relative humidity ($R^2 = 0.51$), vapor pressure ($R^2 = 0.53$), remaining ratio ($R^2 = 0.52$), and remaining water isotopes ($R^2 = 0.61$) were even stronger than for $\delta^{18}O$.

[Figure 4: see original paper]
[Figure 5: see original paper]

3. Conclusions

This study designed an evaporation pan experiment based on isotopic mass balance and the Craig-Gordon linear resistance model to simulate atmospheric water vapor isotopic composition concurrent with evaporation processes. Using actual atmospheric vapor isotope monitoring data, we evaluated model reliability and reached the following conclusions:

1) During the experimental period, simulated atmospheric water vapor isotopes based on the evaporation pan experiment reflected actual atmospheric vapor isotope variations. Simulated $\delta^{18}O$ showed good consistency with measured values (RMSE = 4.5‰, MAE = 3.2‰, MBE = 0.03‰), demonstrating that evaporation pan experiments can provide relatively accurate atmospheric vapor isotopic compositions when temperature and relative humidity are known, which is valuable for precipitation-scarce regions.

2) Sensitivity analysis revealed that temperature effects on the model were smaller than relative humidity effects under equivalent standard deviation changes. The model showed asymmetric sensitivity to remaining ratio changes, with increased sensitivity when the remaining ratio increased. Relative humidity, remaining ratio, and remaining water isotopic values all correlated with simulation residuals.

3) When relative humidity was below 60%, simulation residual distribution became more dispersed. In the final experimental stage, reduced remain-

ing water volume and enriched heavy isotopes in the remaining water corresponded to larger water vapor isotope simulation residuals.

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