

Response to Reviewers

We sincerely appreciate the insightful comments and constructive suggestions from both reviewers, which have significantly improved the clarity and robustness of our methodology. We also thank the reviewers for their positive and encouraging feedback.

In this response letter, we have addressed each comment in detail below. Our responses are highlighted in **blue**, with corresponding revisions in the manuscript also indicated in *blue italics*. All line numbers in this document refer to the updated version of the manuscript.

Thank you for your time and consideration.

With best regards,
Di WANG
On behalf of all authors

AC1: 'Comment on amt-2024-151', 16 Dec 2024

This manuscript describes methods by which to interpret isotope and humidity data from drone-mounted permeable gas sampling bags. The conceptual model appears to be generally useful for inferring atmospheric conditions based on gas composition inside sampling bags. However, the conceptual derivation of the model should be more robustly described, improving precision of communication but especially considering all relevant effects such as temperature and pressure. There is also a lot of improvement needed in precision of notation and terminology, such as the definition of diffusion, silent substitution of delta notation for isotopic ratio in a key equation, and others that I have noted below in the detailed comments. Finally, the actual sampling techniques are not described, so the example drone flight profile is difficult to interpret.

We appreciate the reviewer's thoughtful evaluation of our study and the detailed suggestions provided. Your feedback has helped us refine the conceptual model, improve the clarity of our manuscript. We have strengthened the conceptual derivation of the model, improved the notation and terminology for consistency, and provided a more detailed description of the sampling techniques. Below, we address each comment in detail.

L90 differential diffusion does cause fractionation, but they are not synonymous.

To avoid ambiguity, we have revised the sentence as follows (lines 91-92):

"This differential diffusion, can alter the original isotopic composition of the collected air samples."

L90 there are two relevant gradients causing fractionation: one in concentration of water (causing mass flux), and one in isotopic composition (resulting in no net mass flux). The latter can cause fractionation even if humidity is the same inside and outside of the bag. Neglecting the second gradient may be justified if it is small, but it should

not be ignored completely by the theoretical derivation.

We acknowledge that the role of isotopic composition gradients was not explicitly stated in the Introduction. To address this, we have added the following clarification (lines 92-93):

“Moreover, differential diffusion can also occur due to gradients in isotopic composition.”

Additionally, we would like to point out that our model (Eq. 8) accounts for both the concentration gradient ($q_e - q(t)$) and the isotopic composition gradient ($R_e - R(t)$).

L125 I have several comments about Eq 1:

it neglects effects of pressure and temperature differences across the bag membrane. (2) wouldn't it be more general to formulate this equation in terms of partial pressure of water vapor instead of mass concentrations? That would partially resolve #1

We appreciate the reviewer's insightful comments.

Regarding pressure and temperature differences across the bag membrane:

The air bags were stored and measured in a temperature-controlled chamber, ensuring stable temperature conditions throughout the experiment (lines 226-228). Internal and external pressures were equal to atmospheric pressure, meaning no pressure gradient existed across the bag membrane. To clarify this, we have explicitly stated the boundary conditions and assumptions under which Equations (1) and (2) hold (lines 139-142):

“The validity of Equation (1) and (2) relies on the assumptions that internal and external pressures remain equal to atmospheric pressure, ensuring no pressure gradient across the bag membrane, that the internal vapor is well-mixed, and that the exchange rate follows a first-order process. Additionally, if the temperature remains constant, k and k_i are assumed to be constant.”

Regarding the use of partial pressure instead of mass concentration:

This is indeed a valuable approach that could enhance the general applicability of the model, particularly under conditions where pressure and temperature gradients exist across the bag membrane. Under our experimental setup, where temperature is stable and internal and external pressures are equal, mass concentration and partial pressure are directly proportional. As a result, using mass concentration is fully consistent with our experimental conditions. This formulation simplifies the parameterization and is more convenient for comparison with direct humidity measurements. We fully agree that future work could extend the model to incorporate varying pressure and temperature conditions, where a formulation based on partial pressure would be more appropriate. We have noted this as a potential future direction in the revised manuscript (lines 635-638):

“This study was conducted under stable temperature and equal internal and external pressures during storage. We acknowledge that a formulation based on partial pressure of water vapor would be more general and could improve model applicability under varying temperature and pressure conditions. Future work could extend the

model to account for these factors.”

L124 It's not flux toward the bag, but into the bag, correct?

The phrase "The flux of water toward the bag " has been modified to "The flux of water into the bag" to correctly describe the direction of water movement (line 127).

defining k in g/kg adds a potentially confusing dimensionality to k , so it is not dimensionless as might be assumed and so that F takes on the units of g/m²/s instead of the si base units kg/m²/s that readers might assume without reading carefully. Maybe there is a good reason for the choice; please tell us.

We appreciate your comment. To ensure consistency with SI units, we have adjusted the units of the parameters in this equation. Specifically, we changed the units of $q(t)$ (the variation of humidity inside the air bag over time) and q_e (the environmental humidity) from g/kg to kg/kg (lines 127-131).

To reflect this change, we revised the equation as follows:

“The flux of water into the bag, F (in kg/m²/s), is expressed as:

$$F = k * (q_e - q(t)) \quad (1)$$

where $q(t)$ represents the variation of humidity inside the air bag over time (in kg/kg), q_e denotes the environmental humidity (in kg/kg), k is water vapor conductance.”

L133 and L141 the definitions of α and λ are both crucial equations. Assigning them equation numbers would make them easier to find.

We have now assigned equation numbers to the definitions of α and λ in the revised manuscript to improve clarity and accessibility (lines 138 and 154).

L139 the mass balance assumptions are not clear. How can M be constant if there is water flux into the bag? Does this mean we must assume that all vapor transport into the bag is balanced by an equal mass of non-water vapor transport out of the bag? Or maybe this theory only works if dM/dq is very small? What are the limits of this assumption?

We sincerely appreciate the reviewer’s insightful question regarding the mass balance assumption. The assumption that M remains constant is based on the fact that specific humidity (q , in kg/kg) is much smaller than 1, meaning water vapor contributes only a small fraction of the total air mass. Even under extreme conditions, q varies from approximately 0.5×10^{-3} (0.1%) to 13×10^{-3} (1.3%) along the vertical profile, leading to a maximum mass variation of ~1%. This variation is negligible compared to the total air mass, making the assumption of constant M a reasonable approximation.

To improve clarity, we have revised the manuscript as follows (lines 149-150):

“Assuming that M is constant, which is reasonable given that the total mass variation due to water vapor flux is at most 1%.”

L141 this definition of λ can be loosely defined as a diffusion coefficient, but it is probably better termed (non-dimensional) conductance. It defines the rate of net mass flux in response to a gradient in concentration, but neglects gradients in pressure,

temperature, and isotopic composition. A standard definition of a diffusion coefficient would have dimensions cm²/s. Further confusion arises in sec 3.2, where lambda is called "permeability" L218. Please choose consistent terms.

We appreciate the reviewer's clarification regarding terminology. To improve consistency and precision, we have standardized the nomenclature throughout the manuscript as follows:

- 1) k is now referred to as water vapor conductance.
- 2) k_i is now referred to as isotopic conductance.
- 3) λ (= k*A/M) is now consistently referred to as the water vapor exchange coefficient, incorporating both the exchange area and the air mass inside the bag.
- 4) λ/α is now consistently referred to as the isotopic exchange coefficient.

L167 it would be helpful to be extra clear here that the alphas being obtained are those due to fractionation due to mass flow through bags.

We accepted your suggestion and have revised the sentence as follows (lines 182-183):

"Knowing λ, we can deduce the isotopic fractionation coefficient due to fractionation caused by mass flow through bags, α, for each isotope."

L181-183 there is a lack of clarity here in notation. Delta 18O and delta 2H do not appear in eq 11. Substituting delta notation for ratio notation has no consequences for the alpha in Eq 11 because the standard ratio cancels out, but it would be kinder to readers to justify the use of delta notation either by deriving Eq 11 in terms of deltas or to explain here that ratios of R and ratios of deltas are equivalent.

We appreciate the reviewer's suggestion for improving clarity in the notation. To maintain mathematical consistency and align with standard fractionation factor definitions, we use isotope ratios (R) instead of δ-values in equations. To improve accessibility for readers, we have modified and included the following explanation in the manuscript (lines 198-216):

"The constants (λ, α¹⁸O, α²H) can be determined through laboratory experiments and Eqs. 10 and 13 (see Subsection 3.2 and 4.1). If we know the initial values within the air bag (q₀, R¹⁸O₀, R²H₀), the ambient values (q_e, R¹⁸O_e, R²H_e), and the storage time (T_{storage}) of the sampling bag, we are able to simulate the variations in humidity and isotopic ratios inside the air bag according to Eqs. 5 and 8. Similarly, if we know T_{storage}, the humidity and isotopic values at time t = T_{storage} (q(T_{storage}), R¹⁸O(T_{storage}), R²H(T_{storage})) in the air bag, and the ambient values, we can deduce the initial values in the air bag at t = 0 by back-calculating. The equation used for reconstructing the initial isotope ratio (R₀) is:

$$\begin{aligned}
 R_0 &= R_{measured} - \int_0^{T_{storage}} \frac{dR(t)}{dt} dt \\
 &= R_{measured} - \int_0^{T_{storage}} \left(\frac{\lambda}{\alpha} * (R_e - R(t)) + \frac{\lambda}{q(t)} * (q_e - q(t)) * \left(\frac{R_e}{\alpha} - R(t) \right) \right) dt
 \end{aligned}$$

(14)

where R_0 represents the initial isotopic ratio we want to reconstruct, R_{measured} is the observed isotopic ratio after T_{storage} , and $\frac{dR(t)}{dt}$ is defined in Equation (8).

This approach allows us to correct for diffusion-induced isotopic shifts and reconstruct the original vapor composition.

For mathematical clarity and consistency, isotopic ratios (R) are used in the equations presented in previous sections. Replacing R with δ -values would only shift the physical basis without affecting the mathematical validity of the equations or the estimation of α , as the standard ratio cancels out. For clearer visualization, δ -values are used for numerical applications and in the subsequent figures and tables."

L202 flow rate is not measured in psi.

We have added the following clarification (lines 230-233):

"In the measurement procedure, we first activated the dry air cylinder and adjusted the pressure reducing valve to 2 psi (pounds of force per square inch), within the Picarro water isotope analyzer's recommended range of 2–4 psi for carrier gas. Due to built-in flow regulation, the instrument maintains a gas flow rate of 30–50 mL/min."

L209 "can" or "did"? And what is a parallel sample?

We have revised "can achieve" to "achieved" for accuracy and replaced "parallel samples" with "replicate samples—air samples collected simultaneously under the same conditions" for clarity.

L210 I'm not following—which bias is this? I am guessing this is in the laser spec, but it would be nice to be clear.

We have clarified that the correction addresses isotope measurement bias due to the instrument's sensitivity to water vapor concentration (lines 242-243):

"To correct the isotope measurement bias caused by the instrument's sensitivity to different water vapor concentrations (Schmidt et al., 2010)"

L210 this paragraph is difficult to follow because it appears to use jargon specific to the piece of equipment used (but not fully specified—was it a Picarro A0101?).

We have revised the paragraph for clarity and explicitly provided the specific model of the Picarro analyzer. The updated text now states (lines 242-247):

"To correct isotope measurement bias caused by the instrument's sensitivity to different water vapor concentrations (Schmidt et al., 2010), we used the built-in Standard Delivery Module (SDM) of the Picarro 2130i water vapor isotope analyzer to generate a 500–25,000 ppm water vapor gradient for isotope measurements. We selected 20,000 ppm as a reference humidity level, as this corresponds to the optimal accuracy range of the Picarro analyzer (JingfengLiu et al., 2014; Schmidt et al., 2010)."

Table 2.1 is not needed

We have moved the table to Appendix A.

L228 α_{δ} is an unfortunate choice in nomenclature. The standard variable is α , which can be made more specific by listing the isotopes involved (eg $\alpha_{H2/H1}$), but it adds only confusion to add " δ " because the δ notation has nothing to do with the isotope fractionation factor. α is defined in terms of isotopic ratios (i.e., not in terms of δ).

To avoid confusion, we have revised the notation as follows:

$$\alpha_{\delta} \rightarrow \alpha$$

$$\alpha_{\delta^{18}O} \rightarrow \alpha_{^{18}O}$$

$$\alpha_{\delta^2H} \rightarrow \alpha_{^2H}$$

L232 injected how? Liquid? This is $\sim 10^{-2}$ ml, correct? L255 And 10^{-3} ml in experiment 3? I'm surprised this was easier than using lab air and later adjusting the humidity or isotopic composition of a testing chamber.

We have supplemented the manuscript with a detailed explanation of how reference air bags with known water vapor isotopic values were prepared. The revised text now states (lines 267-274):

“Empty, clean air bags were first filled with dry air, then sealed by closing the bag valve. To maintain a closed system while injecting reference water, a dedicated injection septum was installed on the valve. After reopening the valve, a fixed amount of laboratory reference liquid water with known isotopic values was injected into the dry air-filled bag using a 10 μ L injection needle. In Experiment No. 2, we ensured that the initial humidity (q_0) was approximately equal to the environmental humidity (q_e). To ensure $q_0 = q_e$, the environmental vapor concentration was first measured, followed by the calculation and experimental determination of the water volume to be injected into the air bag.”

We also have revised the text to include the specific amounts of water injected and the isotopic values used (lines 293-299):

*“To validate the diffusion model under diverse conditions and evaluate its uncertainties, we repeated Experiment No. 2, but injected different amounts of water with known isotopic values to achieve a range of humidities from approximately $1/8 * q_e$ to q_e . Using the method described in Experiment No. 2, we injected 6 to 50 μ L of reference water into a 4L air bag filled with dry air to achieve the desired humidity range. Additionally, we repeated the experiment using two reference waters with distinct isotopic compositions, specifically $\delta^{18}O = -58.82\%$, $\delta^2H = -428.82\%$ and $\delta^{18}O = -29.89\%$, $\delta^2H = -222.89\%$.”*

L259 "can" or "did"?

We have revised "can used" to "used" for accuracy.

L266-268 the logic of how the sampling system works is important. Full details might not be appropriate here, but a citation to them would be nice. At minimum I would expect an outline of how it works, given that understanding the results depends on

understanding the methods.

We appreciate your suggestion and have supplemented the paragraph with a more detailed description of the sampling system (lines 311-317):

“We designed and built a collection module for fixed-height sampling, incorporating diaphragm vacuum pumps, a rudder mounted on the drone, and a control module linked to a remote operating system. When the drone reaches a specified altitude, we remotely activate the designated air pump to inflate a specific air bag. Once sampling is complete, the pump is deactivated, and the drone ascends to the next target altitude, where the corresponding air pump inflates another air bag. This process was repeated until all predetermined samples were collected.”

We also have provided more details about the drone flight path and sampling strategy in the following paragraph (lines 328-337):

“We collected water vapor samples every 500 meters, starting from near the surface along the vertical profile. To optimize sampling across different altitude ranges, we deployed UAVs designed for varying flight altitudes. Generally, the UAV operating at lower altitudes collected samples at seven heights from 4,000 to 7,000 meters in a single flight. The mid-altitude UAV collected samples at four heights from 7,500 to 9,000 meters in one flight, while the high-altitude UAV collected samples at four heights from 9,500 to 11,000 meters in two flights. Each flight took approximately 20~30 minutes. In case of any disruptions during sampling, we repeated the process until a complete vertical profile was obtained. At the beginning of the experiment, we also collected replicate samples at each height to ensure data consistency.”

L269 of course the bags do not deflate because of mass loss, but because of increased pressure outside the bag, and the pressing danger would therefore seem to be preventing ingress of new air, not egress of sample. Do the one-way valves protect against this?

We appreciate the reviewer for pointing out our oversight in our writing and raising the concern about air ingress. To address this, we have added details about the vacuum diaphragm pump (lines 317-323):

“Self-sealing diaphragm vacuum pumps were used to transfer air into the sampling bags. Once the pump ceased operation, it remained sealed from the external environment, preventing unintended air ingress. Additionally, due to the flexible nature of the air bags, internal and external pressures remained balanced. As air pressure increases during the drone's descent after collection. To further prevent the loss of collected air samples, a one-way valve was installed to block backflow. Additionally, the one-way valve helps prevent large droplets from entering the air bag during the collection process.”

L280 the vapor is not measured in situ. Samples are removed from their locations and measured elsewhere.

We appreciate the reviewer's clarification. To clarify our analysis procedure, we revised Lines 337-339 as follows:

“By integrating high-altitude drone sampling with subsequent water vapor isotope

analysis using the Picarro analyzer at the surface, we obtained vapor isotopic profiles up to an altitude of 11 km.”

L287 this sentence illustrates what I mean in my comment L266: readers cannot appreciate the sampling environment in any useful detail, so there is no way to fully understand why, for example, "it is difficult to experimentally estimate λ for different altitudes".

We have supplemented the paragraph with a more detailed description of the sampling system and strategy in response to Comment L266.

Here, we further clarify that we estimate M at high altitudes to determine λ_{alt} , while avoiding potentially confusing expressions (lines 345-350):

“ λ is defined as $k \cdot A/M$ and depends on the air mass M in the bag. In drone-based vertical sampling, M varies with altitude due to pressure changes, requiring an estimate of λ for different altitudes (λ_{alt}). However, since λ is an intrinsic property of the bag material, its apparent variation reflects uncertainties in estimating collected M, which depend on atmospheric pressure (P), sampling time, and pump efficiency (ϵ):

$$M_{alt} = M_{surface} * \frac{P_{surface}}{P_{alt}} * \frac{Sampling\ time_{alt}}{Sampling\ time_{surface}} * \epsilon \quad (15)$$

L291 longer sampling time where? To collect the air or to analyze the samples?

To specify that the extended sampling time applies to air collection at higher altitudes, we have revised the sentence as follows (lines 353-355):

“To compensate for this effect, a longer sampling time was used to collect air at higher altitudes (Sampling time_{alt}) than at the surface (Sampling time_{surface}) (Fig. A1).”

In general, section 3.4.1 seems to all collapse to "mass was estimated proportional to pressure at the sampling altitude and pumping time". The overly detailed presentation makes the logic seem more complicated than it is.

We have simplified Section 3.4.1 to improve clarity and avoid unnecessary complexity (lines 344-363):

“3.4.1 Estimating the air mass in the bag

λ is defined as $k \cdot A/M$ and depends on the air mass M in the bag. In drone-based vertical sampling, M varies with altitude due to pressure changes, requiring an estimate of λ for different altitudes (λ_{alt}). However, since λ is an intrinsic property of the bag material, its apparent variation reflects uncertainties in estimating collected M, which depend on atmospheric pressure (P), sampling time, and pump efficiency (ϵ):

$$M_{alt} = M_{surface} * \frac{P_{surface}}{P_{alt}} * \frac{Sampling\ time_{alt}}{Sampling\ time_{surface}} * \epsilon \quad (15)$$

where M_{alt} is the air mass collected at a different altitude and $M_{surface}$ represents the air mass collected at the surface. At higher altitudes, where the air pressure (P_{alt}) is lower than at the surface ($P_{surface}$), less air will be pumped into the air bag. To compensate for this effect, a longer sampling time was used to collect air at higher altitudes (Sampling time_{alt}) than at the surface (Sampling time_{surface}) (Fig.A1).

Given that λ_{alt} is proportional to M_{alt} , we calculated it as:

$$\lambda_{alt} = \lambda_{surface} * \frac{P_{surface}}{P_{alt}} * \frac{Sampling\ time_{alt}}{Sampling\ time_{surface}} * \epsilon \quad (16)$$

where $\lambda_{surface}$ is the λ quantified experimentally at the surface.

Since air pressure and sampling times were directly measured, the primary source of error for M_{alt} , and consequently λ_{alt} , arises from pump efficiency (ϵ), which may decrease over time and at lower pressures. Using the estimated λ_{alt} , the observed vertical isotope profiles were corrected based on Eq.14 from Section 2.2. The uncertainty estimation is discussed in Section 3.4.2.”

L306 comment 1: what does "diffusion model correction process" mean? Parameterization? Correction of model structure?

We corrected ‘Potential sources of error in the diffusion model correction process’ to ‘Potential sources of error in correcting vertical observations using the diffusion model’ (line 365).

L306 comment 2: I don't think lambda_surface and lambda_alt are proper variables. Lambda is a property of a bag that should not depend on altitude. Its apparent dependence on altitude in this work is due to errors estimating masses. Therefore, unless I am missing something, the better variable to report here as a source of error is the estimate of air mass.

We completely agree with the reviewer. The variation in λ at different altitudes is not due to an inherent altitude dependence but rather results from errors in estimating M . We have revised the manuscript to emphasize that λ_{alt} is derived directly from $\lambda_{surface}$, pressure, sampling time, and pump efficiency (ϵ), as shown in Eq.16 (Section 3.4.1):

$$\lambda_{alt} = \lambda_{surface} * \frac{P_{surface}}{P_{alt}} * \frac{Sampling\ time_{alt}}{Sampling\ time_{surface}} * \epsilon$$

Since air pressure at different altitudes is well-defined and sampling time is accurately recorded, these parameters do not contribute to uncertainty. Instead, the primary source of error stems from variations in pump efficiency (ϵ), which directly affects M_{alt} and, consequently, λ_{alt} .

Therefore, we now explicitly identify the uncertainty in λ_{alt} is fully propagated from the uncertainties in $\lambda_{surface}$ and ϵ , rather than being treated as an independent source of error. We have revised the manuscript accordingly to reflect this clarification (lines 344-363). The full details of the corresponding revision can be found in our response to the comment above.

L306 comment 3: mismatches between model and data are not sources of error, they are themselves the error.

We appreciate the reviewer’s clarification. We have revised the manuscript to distinguish error sources from model-data mismatches. For example, in lines 365-366:

“Potential errors in correcting vertical profiles using the diffusion model include estimates of $\lambda_{surface}$, α , Sampling time_{alt}, and mismatches between model and experiments (Table 1).”

Sec 3.4.2 the uncertainty section is difficult to follow and needs a revision for conciseness and clarity. The section includes too much information (e.g., how mean parameter estimates were obtained—i.e., nothing to do with uncertainty), is not well organized, and is also not always specific when it needs to be. An example of this last point is the $\frac{1}{4}$ estimate for pumping time. Is this really uncertain to that degree? It seems more likely (lacking actual experimental details), that pumping time is well known and the real variable is mass captured.

We appreciate the reviewer's feedback and have revised Section 3.4.2 for improved clarity and conciseness. We have removed unrelated details while retaining necessary information and reorganized it for better readability (lines 364-390):

“3.4.2 The method of uncertainty estimation

Potential errors in correcting vertical profiles using the diffusion model include estimates of λ_{surface} , α , pump efficiency (ϵ), and mismatches between model and experiments (Table 1). We detail each below:

1) λ_{surface} uncertainty: laboratory experiments provided upper and lower bounds on λ_{surface} (Subsection 4.1). These were used for error estimation.

2) α uncertainty: the λ and λ/α were first estimated from several experiments, from which α was calculated. Their averaged values were used separately to parameterize the model. As highlighted in Subection 3.2.2, estimating λ/α (and subsequently calculating α) requires results from cases where q_0 equals q_e , minor variations in q_0 and fluctuations in q_e could introduce non-systematic discrepancies between the model and experimental results. Consequently, for analyzing the contribution of α to uncertainties, only α values derived from experiments where the model closely matched the majority of experimental results were considered. Selection criteria for these experiments included minimal deviation between q_0 and q_e , minimal deviation between experimental data and simulations, and stable q_e values, ensuring the reliability of the chosen α .

3) Pump efficiency (ϵ) uncertainty: The efficiency of the pump may decline over time or vary with atmospheric pressure, affecting the collected air mass M . To account for this, we applied a conservative uncertainty range of 0.75 to 1.25 relative to surface conditions, ensuring the full range of possible variations in M_{alt} was considered.

4) Model-experiment mismatches: We compared model simulations with experimental data across 87 cases, calculating the average absolute discrepancy. These mismatches were included as an additional uncertainty component.

Total Uncertainty Calculation: The maximum discrepancy across all calibration results—using the full uncertainty range for λ_{surface} , α , and pump efficiency (ϵ)—was determined. The model-experiment mismatch was then added as an independent error component. The final uncertainty estimates, reported in Subsections 4.3 to 4.5, account for all potential error.”

L376 this temperature (and pressure) dependence should be recognized in the theoretical development.

We have revised the text to explicitly acknowledge the temperature and pressure dependence (lines 433-440):

“The specific parameter values obtained in this study pertain to the Teflon air bags used in the aforementioned tests, conducted at an ambient temperature of 16°C. These values depend on bag material, temperature, and pressure, which should be considered when applying the model under different conditions. We also noted batch-to-batch variations among air bags from the same manufacturer. We apply α measured under ground-level storage and measurement conditions, assuming negligible temperature and pressure effects during the short (10–20 min) drone-based sampling period. Future work is needed to quantify these dependencies.”

Fig 3 it would improve the accessibility if the caption told us which experiment these data come from

We have revised the figure caption to specify the corresponding experiments (line 441):

“Figure 3 Determination of 3 parameters of the diffusion model : λ_{surface} (a) from Experiment No. 1, $\alpha_{\text{ }^{18}\text{O}}$ (b), and $\alpha_{\text{ }^2\text{H}}$ (c) from Experiment No. 2.”

Fig 4a misspelling of Environment. Also, Environment should be defined in the main legend, not in each panel

We have corrected the misspelling of "Environment" in Fig. 4a and moved its definition to the main legend:

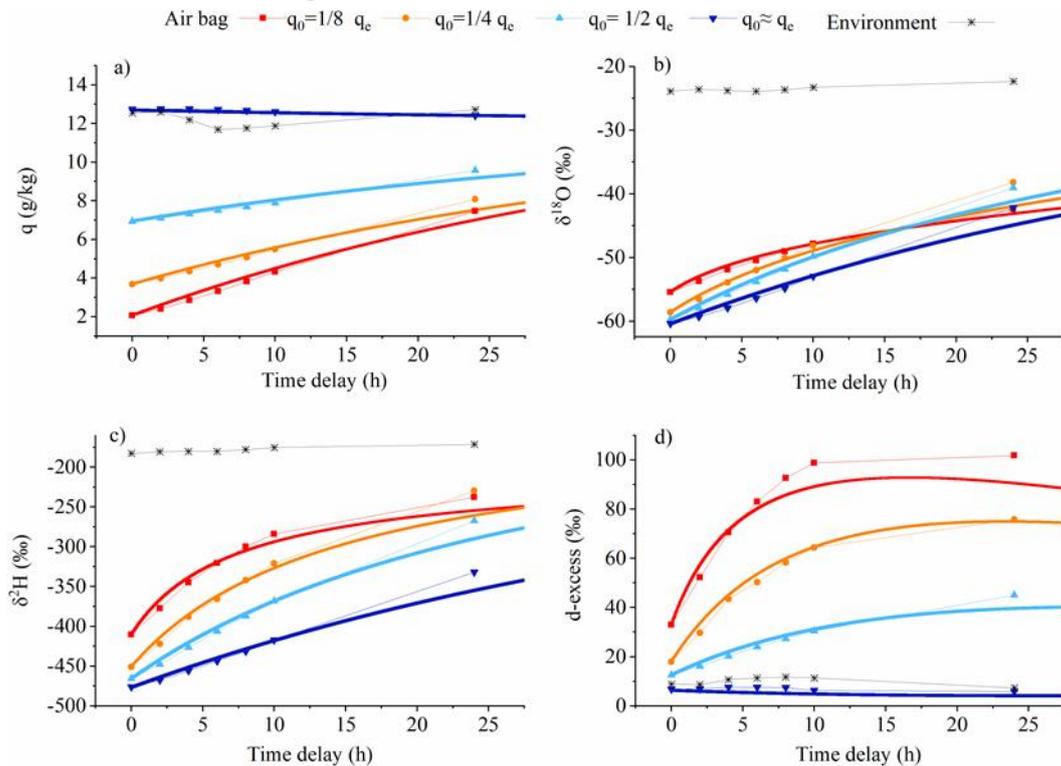


Fig 4 I don't understand why the isotopic equilibration models cross over each other at long time. What equation exactly generates the solid lines model fits?

We appreciate the reviewer's question. We now provide an interpretation of this unexpected result. To achieve this, we slightly modified the final form of Eq. 8 to isolate

two terms: the first term drives $R_{(t)}$ towards R_e at a constant rate, while the second term drives $R_{(t)}$ towards R_e/α at a rate dependent on $(q_e - q)$ (line 163).

$$\frac{dR(t)}{dt} = \frac{\lambda}{\alpha} * (R_e - R(t)) + \frac{\lambda}{q(t)} * (q_e - q(t)) * \left(\frac{R_e}{\alpha} - R(t)\right) \quad (8)$$

We have added the following discussion in the manuscript (lines 459-466):

“We observe that some curves unexpectedly intersect, which can be understood by analyzing Eq. (8). The first term $(\frac{\lambda}{\alpha}(R_e - R_{(t)}))$ continuously drives $R_{(t)}$ towards R_e , while the second term $(\frac{\lambda}{q(t)}(q_e - q_{(t)})(\frac{R_e}{\alpha} - R_{(t)}))$ modulates the rate of change. Initially, for simulations with lower q_0 values (e.g., the red and orange curves), $q_e - q_{(t)}$ is large, making the second term significant and positive, thereby increasing $R_{(t)}$ more rapidly. However, as $R_{(t)}$ exceeds R_e/α , the sign of this term reverses, slowing down the increase in $R_{(t)}$ compared to other curves. In contrast, curves with higher initial q_0 values (e.g., blue curve) experience a steadier growth and eventually surpass the initially faster-growing curves, leading to the observed crossing.”

Regarding the equation governing the solid lines in Fig. 4, we have clarified this in the manuscript (lines 198-211 and 301-309). The model fits are generated using Eqs. (5) and (8), with parameters obtained from Experiments No. 1 and 2. Additionally, we revised the figure description to explicitly distinguish the meaning of solid lines (simulations) and markers (experimental observations) (lines 447-450).

(lines 198-211) “The constants $(\lambda, \alpha_{^{18}O}, \alpha_{^2H})$ can be determined through laboratory experiments and Equations 10 and 13 (see Subsection 3.2 and 4.1). If we know the initial values within the air bag $(q_0, R_{^{18}O_0}, R_{^2H_0})$, the ambient values $(q_e, R_{^{18}O_e}, R_{^2H_e})$, and the storage time $(T_{storage})$ of the sampling bag, we are able to simulate the variations in humidity and isotopic ratios inside the air bag according to Eqs. 5 and 8. Similarly, if we know $T_{storage}$, the humidity and isotopic values at time $t = T_{storage}$ $(q(T_{storage}), R_{^{18}O(T_{storage})}, R_{^2H(T_{storage})})$ in the air bag, and the ambient values, we can deduce the initial values in the air bag at $t = 0$ by back-calculating. The equation used for reconstructing the initial isotope ratio (R_0) is:

$$\begin{aligned} R_0 &= R_{measured} - \int_0^{T_{storage}} \frac{dR(t)}{dt} dt \\ &= R_{measured} - \int_0^{T_{storage}} \left(\frac{\lambda}{\alpha} * (R_e - R(t)) + \frac{\lambda}{q(t)} * (q_e - q(t)) * \left(\frac{R_e}{\alpha} - R(t) \right) \right) dt \end{aligned} \quad (14)$$

where R_0 represents the initial isotopic ratio we want to reconstruct, $R_{measured}$ is the observed isotopic ratio after $T_{storage}$, and $\frac{dR(t)}{dt}$ is defined in Eq.8.

This approach allows us to correct for diffusion-induced isotopic shifts and reconstruct the original vapor composition.”

(lines 301-309) “Once the parameters of the diffusion model have been obtained through Experiments No. 1 and 2, we used this model to simulate the variations in water vapor humidity and isotope values inside the air bag over time for Experiments No. 2 and 3 (refer to Section 2). When simulating these experiments using the diffusion model, we used measurements taken after a 5-minute delay as the initial condition to ensure that it represented complete evaporation of the injected water. We then simulated the temporal variations in humidity and vapor isotopes within the air bag using a 5-minute time step using Eqs.5 and 8, separately. The resulting outputs (hereafter referred to as 'the diffusion model simulations') will be shown in Subsection 4.2 and code are available as supplementary material.”

(lines 447-450) “The simulations from our diffusion model (lines in Figs. 4, 5, 6, and Fig. S2) are in close agreement with our experimental observations (markers in Figs. 4, 5, 6, and Fig. S2), showing consistency in humidity, $\delta^{18}\text{O}$, $\delta^2\text{H}$, and d-excess variations, with only minor deviations.”

L398 should specify HD16O—or omit it, since the sentence is about 18O

We have revised HDO to HD¹⁶O for accuracy.

Fig 5 delete "(a, b) (a-b)" at the beginning of the caption

We have removed it.

Fig 5 is difficult to follow. What is "real value"--it looks like initial isotopic composition inside the bag, but why does it not change with time and why is it measured at different times compared to the colored dots? What equation exactly generates the solid lines model fits?

We have revised "real value" to "Reference: initial values inside the air bag" for clarity. This value is also plotted at different times to serve as a reference for comparing changes in the air bag over time. We have also revised the legend of Fig. 5 accordingly.

As stated in our response to comments on Fig. 4, we have provided a relevant description in the manuscript (lines 198-211 and 301-309) regarding the equation used to generate the lines model fits. Additionally, we have explicitly clarified the meaning of the lines and markers in the caption of Fig. 5 (line 467):

For figures 4 and 5, plotting the humidity inside the bags over time would help a lot in illustrating the processes and ensuring the models are describing the processes correctly.

We appreciate the reviewer’s suggestion. Figure 4a already presents humidity inside the bags over time, and we have additionally provided this information for Figures 5 and 6 in Supplementary Figure S2.

We have also clarified this in the manuscript (lines 447-450):

“To validate the model, we used Experiment No.3 described in Subsection 3.2. The simulations from our diffusion model (lines in Figs. 4, 5, 6, and Fig. S2) are in close agreement with our experimental observations (markers in Figs. 4, 5, 6, and Fig. S2), showing consistency in humidity, $\delta^{18}\text{O}$, $\delta^2\text{H}$, and d-excess variations, with only minor deviations.”

For figures 5 and 6, I appreciate the idea to diagram the processes, but I found the diagrams unhelpful because they illustrate only the magnitudes of fluxes and ignore the crucial differences in humidity inside the bag.

To clarify the role of humidity differences inside and outside the air bag, we have revised the figure captions to explicitly highlight the impact of q_0 vs. q_e on isotopic evolution (lines 467 and 490):

“Figure 5 (a-b) Variations of $\delta^{18}O$ under different conditions: (a) when both the differences between internal ($\delta^{18}O_0$) and external ($\delta^{18}O_e$) $\delta^{18}O$ values as well as between internal (q_0) and external (q_e) humidity are not significant, $\delta^{18}O$ gradually increases toward equilibrium; (b) when q_0 is significantly lower than q_e , a stronger vapor influx causes enhanced kinetic fractionation, leading to a decrease in $\delta^{18}O$. (c-d) Corresponding schematics: (c) illustrates the mechanism for (a), where a weaker humidity gradient results in slower isotopic shifts, while (d) corresponds to (b), showing intensified fractionation with a larger gradient, with arrows indicating vapor flux direction and fractionation intensity. $\delta^{18}O(t)$ is the variation of $\delta^{18}O$ within the air bag over time. In (a) and (b), the colored lines represent diffusion model simulations based on Eq.8, using parameterization from Experiments No. 1 and 2. The square-marker-connected lines indicate the initial values inside the air bag, which remain constant over time and serve as a reference for comparison (legend: Reference).”

“Figure 6 (a-b) Evolution of d-excess in cases: (a) when the difference between the humidity inside (q_0) and outside (q_e) the air bag is not significant, d-excess increases gradually; (b) when q_0 is significantly lower than q_e , a stronger vapor influx enhances kinetic fractionation, causing a more rapid d-excess increase. (c-d) Corresponding schematics: (c) illustrates the mechanism for (a), where a smaller humidity gradient results in slower isotopic shifts, while (d) corresponds to (b), showing intensified fractionation with a larger gradient. d_0 indicates the initial d-excess value at $t = 0$, d_e represents the d-excess in the environment. $d(t)$ denotes the variation of d-excess within the air bag over time.”

L405 referring to Fig 4 as the first scenario and Fig 5 as the second and third scenarios is confusing, because they are not so labeled in the figures and difficult to keep straight in the text.

We appreciate the reviewer’s feedback and have revised the text to improve clarity. Instead of referring to Figures 4, 5 and 6 as specific scenarios, we now explicitly describe the conditions presented in each figure to avoid confusion.

L431 again it would be helpful to be explicit about which equation is "the model"

We have provided a relevant description in the manuscript (lines 198-211 and 301-309) regarding what 'the model' refers to. The full details of the corresponding revision can be found in our response to the comment on Fig. 4.

L441 ok but (1) there are other ways to flag for unrealistic results, so focusing on this one seems odd; and (2) leaving in those six data points would presumably not have

much effect on the results, so this detail seems distracting.

We have removed the following sentences from the manuscript and retained data points with d-excess values less than 1‰:

“In this dataset, acquired from the drone observations and subsequently corrected using the diffusion modeling, data points with d-excess values less than 1‰ were omitted, as these values are unrealistic and likely result from overcorrection of the δ -values. This resulted in the exclusion of 6 out of 1039 samples.”

This revision only affects a very small number of data points (6 out of 1039), and including these data does not alter the overall results and conclusions.

Minor global comment: the word "value" is redundant almost everywhere.

We have reviewed the manuscript and removed redundant instances of "value" for conciseness while retaining necessary ones for clarity.

L456 "model corrections" can never affect d18O in the bag. I think this is saying that applying corrections for vapor pressure differential and fractionation by the bag changes the estimate of the atmospheric d18O. L454-459 why say all this twice? The correction process is the same for 2H and 18O, and the d response follows. This description makes it sound more complicated than that.

We appreciate the reviewer's clarification and have revised the text to eliminate redundancy and improve clarity (lines 526-531):

“The strong kinetic fractionation driven by the diffusion of air into the air bag results in a decrease in the water vapor $\delta^{18}\text{O}$ within the bag. After applying model corrections, the corrected $\delta^{18}\text{O}$ values inside the bag increased slightly compared to pre-correction levels. As described in Subsection 4.2, vapor flux with higher d-excess entering the bag increases the d-excess inside. As a compensation, the diffusion model applies corrections, resulting in a reduced d-excess value after correction (Fig. 7c and 10).”

Fig 10 it is not clear what "Picarro" means here. Is this the measurement of ambient vapor at the surface at the time of sampling aloft? Or is this bag samples vs. satellite-inferred estimates?

We have revised the figure caption (line 576) and related descriptions (lines 577-579):

(line 576) "(a, b) Raw and corrected (with uncertainties) altitude-averaged air bag measurements from 3856 m to 4000 m, compared with in-situ surface-level measurements at 3856 m taken by the Picarro (legend: Picarro)."

(lines 577-579) The left panel of Figure 10 (Fig. a, c, and e) shows the comparison of raw and corrected water vapor $\delta^2\text{H}$ measurements at different altitudes with in-situ surface-level measurements on the Picarro or IASI satellite data at corresponding altitudes.

L551 the methods in this manuscript have nothing to do with laser spectrometry; the samples could as well be measured by other methods.

We appreciate the reviewer's clarification and have revised the text to remove unnecessary references to laser spectrometry (lines 629-632):

“Our drone-based sampling system, combined with the diffusion model, effectively addresses the limitations of traditional high-altitude water vapor measurement methods. It meets the need for lightweight equipment while providing a more economical, efficient, and flexible alternative to conventional approaches involving large aircraft, airships, and balloons.”