

Review acp-2024-4

Technical note: Theoretical and experimental investigation of isotopic exchange between water vapour and droplets under isothermal saturation conditions

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The manuscript “Theoretical and experimental investigation of isotopic exchange between water vapour and droplets under isothermal saturation conditions” introduces an approach to estimate the effect of isotopic exchange between water vapour and droplets in saturated conditions on the isotopic composition of water vapour. The theoretical approach allows to calculate the change in isotopic composition of water vapour during this process from environmental factors. The presented data show a similar trend in the isotopic composition from theory and experiment during a time period of 5min.

This study addresses an important question of the effect of isotopic exchange under saturated conditions between droplets and water vapour on the isotopic composition of water vapour. This effect can, for example, not be modeled by the Craig and Gordon (1965) model due to non-linear effects close to saturated conditions. The authors use an interesting experimental approach to test their model. But in its current state, the manuscript does not convincingly show the relevance of their results due to (i) missing definition of the analysed exchange process and how it differs from established terms such as isotopic equilibration between phases, (ii) missing reference to existing models such as equilibrium fractionation factors and Stewart model for the exchange between droplets and water vapour, and (iii) weak statistical analysis without quantitative uncertainty estimates of their experimental and modeled results. In the following, these three main comments are explained in more detail, together with further comments.

Main comments:

- What is the definition of *exchange process*? What is its role for equilibrium fractionation and what is, for example, the difference between equilibration between water vapour and the rain droplets (as e.g. mention on lines 76-77) and the exchange process?
- The experimental results are only compared to the model introduced in this study. It is difficult to relate the results, especially the magnitude of the observed changes in δD and $\delta^{18}O$, to the fractionation effect as simulated by other, existing models (e.g. equilibrium fractionation effect, Craig-Gordon (1965) model, Stewart (1975) model). Some of these model cannot be applied at 100% relative humidity but any discussion of these limitations and how the theoretical approach of this study is filling a gap is missing. The study should outline more clearly how their results relate to previous theoretical models and frameworks.
- Statistical analysis: The discussion of the difference between the experiment and the modeled data focuses mainly on the relative difference between the two datasets. This discussion does not address the uncertainty of the experiment. Do the differences fall within the uncertainty and are the changes during the 300s significant with respect to the differences between different model runs? Further, the cluster analysis is not documented and the interpretation of the clusters as a linear relationship between δD and $\delta^{18}O$ is questionable.

Further comments

- General:
 - The manuscript is often difficult to read due to incomplete sentences, incorrectly used words and grammatical inconsistencies. I do not list all of these issues below, please thoroughly check the language of the manuscript again.
 - The figure captions are often too short. They lack information on the shown data or schematics. Please, improve the captions such that the reader can understand the figures by reading the captions without reading the text.
- Abstract:
 - There are several terms used in the abstract that are not defined/generally known in the field: exchange process (line 17), hydrogen and oxygen isotope line (line 25), the origin (line 25).
 - It is difficult to follow the description of the results in the abstract without having read the manuscript.
- Introduction:
 - Line 62: “in an isotope exchange scenario” do you mean “in an isotope exchange-**only** scenario”
 - Line 67: “Gu et al. 2011” Can you add a reference to earlier work on this topic?
 - Lines 70-71: “kinetic and diffusion fractionation” What is the difference between kinetic and diffusion fractionation?
 - Lines 71-72: “In many cases, the Rayleigh fractionation model is utilised to describe such nonequilibrium processes (Liu et al., 2015)”
 - The Rayleigh model was introduced by Dansgaard (1954)
 - The Rayleigh model describes the evolution of the isotopic composition of water vapour and rain during a rain-out process. This can involve non-equilibrium fractionation if the cloud droplets are forming in over-saturated conditions. But I would not use it as typical example of non-equilibrium fractionation.
 - Lines 76-77: “the isotope exchange process leads to weaker equilibration on the water vapor and precipitation isotope values (Graf et al., 2019)” what do you mean by *weaker equilibration*?
 - Lines 85-87: “The study will deeply our understanding of isotopic changes in the water cycle, especially for coordinated changes in precipitation and water vapour isotopes, and further expand the applicable accuracy and scope of the Rayleigh fractionation model.” Why are results of this study (especially) relevant for the Rayleigh fractionation model?
 - The discussion of literature stays mostly on a macroscopic level without further discussing the processes on a molecular level even though these processes are important in the methods and results section. How has water vapour – droplet interaction been discussed in literature? How does the approach of this study differ from previous approaches?
- Methods and materials
 - In this section, past and present tenses mix and it is not always clear why the tense changes. Please, check again their usage.
 - Fig.1: The schematic of the experiment (green box) is difficult to understand. What are the numbers? What are *Type*? What do the arrows mean?
 - Equation (1): more explanation is needed how equation 1 is derived. What does it represent? Does follow from the assumption that the rate of change in water molecules in the vapour phase and droplets are equal?
 - Equation (4): What is R_r ?
 - Equation (6): What is γ ?
 - Line 166: “significant reduction”: What is a significant reduction? Did you do a statistical test?
 - Line 166-167: “a faster reduction in the specific surface area of the droplets indicated a higher rate of droplet coalescence, which resulted in a significant decrease in water vapour isotopes.” Is this still theoretical or does this refer to the experiment?

- Line 192: “it remains essentially constant” What is “it”?
- Fig.2 caption: “ I includes 1 and 3, II is exchange chamber 4, III includes 9-13, IV includes 2, 5-8 and 14-15)” What are I, II, III and IV?
- Fig. 2: The inlet of the water vapour analysis (5) is above the droplet inlet (3). How do you make sure that the droplets distribute through the entire chamber before they settle?
- Lines 273-274: ”Over 60,000 data points for isotopes and droplet particle sizes were
- produced during the procedure, including 400 liquid water samples.” Why do you mention these numbers? They do not help to understand the outcome of the experiments. It would, e.g. be more useful to know the number of experiment runs.
- Lines 278-279 and lines 283-284: “The characteristic particle size was averaged over
- experimental runs” and “The water vapour isotope data were averaged using the same approach as that used for the aforementioned characteristic particle size.” How was this averaging done? Are all runs averaged to derived mean temporal evolutions of the measured quantities during 300s runs?
- Experiment results and analysis
 - Line 299: “increase/decrease” What does this mean? Please, be more specific.
 - Lines 303-305: This sentence is too long.
 - Fig. 3-5: Do you show means over all experimental runs in Fig. 3-5 means? Can you add a standard deviation (or some uncertainty estimate) around the mean value?
 - Fig. 3: What are the vertical dashed lines in (a)?
 - Fig. 3: The changes in δD and $\delta^{18}O$ are relatively small in this experiment. Is this caused by the small difference in the isotopic composition between droplets and vapour? What magnitude of changes do you expect if the isotopic composition differs more strongly between the droplet and its surrounding?
 - Lines 342-343: “As the droplet size increases, the degree of rare isotope distribution on the surface of the liquid droplets increases, disrupting the previously established equilibrium exchange state.” Why does the distribution of rare isotopes change with an increase in droplet size? What is the assumption on the isotopic distribution in a droplet? Is it well-mixed? Or is there a gradient between surface and inner part of the droplet?
- Discussion
 - Lines 365: “The calculated values” Values of what?
 - Lines 366-368: “The calculated values were averaged based on the number of experimental sets, and the calculated and observed water vapour isotopes during the 109–218 s period were compared (Figure 5).” Why is the model only compared to measurements after 109s? Why does the model not apply to the first period?
 - What is the initial value of δD_D and $\delta^{18}O_D$ in the model?
 - Line 375: “The mean relative errors of water vapour δD and $\delta^{18}O$ showed” Between modeled and measured δD and $\delta^{18}O$?
 - Line 378: “not substantial” What do you mean by *not substantial*?
 - Lines 388-394: The paragraph on relative errors and their discussion is difficult to follow and the meaning of the discussion is not clear. Why is a relative error of 4.5% chosen as reference? How does the relative error help to assess the model performance?
 - Line 408: “ $R^2=1.0$ ”: What is R? And if it is equal to 1, does this mean that all the data points lie perfectly on a line?
 - Line 411: Cluster fitting approach: What is done here? What is the meaning of the clusters? How does this prove a linear relationship between δD and $\delta^{18}O$?
 - Line 445-447: “By integrating the Rayleigh distillation model, this approach holds significant application value for exploring the coordinated changes in precipitation and water vapour isotopes under cooling and saturated conditions.” What do you mean by integrating the Rayleigh model? Is the isotope exchange not already part of the Rayleigh model through the isotopic equilibrium fractionation factor? What do you mean by cooling conditions?

- Conclusions
 - Line 459: “the deviation of hydrogen and oxygen isotope lines from the origin” As in the abstract, what are these lines and the origin?
 - Lines 468-471: Please review the cluster approach: I don’t see how the clusters prove a linear relationship between δD and $\delta^{18}O$.
 - Line 474: “the combined application of the IECEWV and Rayleigh fractionation models” Same comment as above, I don’t understand what you mean by a combination of IECEWV and the Rayleigh model.
- References:
 - Please, check the doi-links in the references. Many links do not work due to a punctuation mark mistake.

Minor comments

- Line 78: quantitatively → do you mean “quantifying”?
- Line 85: deeply → do you mean “deepen”?
- Line 309: specifically → delete
- Line 349: stage → do you mean “plateau”?
- Line 366: in the article → I would refer to the section where you introduce the model.
- Lines 444-445: “In the future, water vapour isotopic values under saturated or near-saturated conditions should be calculated **without** in situ observations by combining this equation with observed raindrop spectral data.” → Do you mean “with in situ observations”?

References:

Craig, H. and Gordon, L.: Deuterium and oxygen 18 variations in the ocean and the marine atmosphere, in: Proceedings of the Stable Isotopes in Oceanographic Studies and Paleotemperatures, 1965.

Dansgaard, W., 1954: The O18-Abundance in fresh water. Geochim. Cosmochim. Acta, 6, 241–260.

Stewart, M. K., 1975: Stable isotope fractionation due to evaporation and isotopic exchange of falling waterdrops : Applications to atmospheric processes and evaporation of lakes. J. Geophys. Res., 80, 1133–1146, doi:10.1029/JC080i009p01133.