Reply to Referee #1

We appreciate the constructive comments and suggestions of Reviewer #1. The provided comments have contributed substantially to improving the paper. Please, find below in black the comments of the reviewer, in blue our responses to the comments and how these comments will be addressed in the revised manuscript.

General Comments:

The manuscript “Triple oxygen isotope systematics of evaporation and mixing processes in a dynamic desert lake system” explores the isotopic dynamics of a terminal lake system in Chile using evaporation pan experiments and Craig-Gordon evaporation modelling. The authors collected samples from numerous small lakes and ponds, groundwater springs, and atmospheric vapour to evaluate the effect of evaporation, sensitivity of input variables for the Craig-Gordon model, and assess the mixing of ponds. The study shows the highly sensitive nature of O17 in ponded water during fractionation and is an assess to partitioning water into mixed and evaporated water pools. I would recommend major revisions to improve the presentation of the manuscript. Three key issues need to be resolved as follows.

Firstly, the objectives and significance of the study are not clearly presented in the introduction. There is a limited introduction to the implication of using oxygen-17 other than “a potentially powerful tool” with much of the remaining introduction on oxygen-17 more suited to a methods section than an introduction. The importance of desert lake systems is central to this manuscript but is has limited emphasis only to oxygen-17. The objectives of the manuscript appeared to be only a sensitivity test of input variables in the Craig-Gordon model rather than assessing the dynamics of the salar system as a whole and using the Craig-Gordon model as a tool. The last part of the introduction seemed to be more of an abstract than an introduction and needs revision.

Thank you for pointing out that the objective of this study becomes not clear in the introduction. We thoroughly revised the introduction and focused on the larger implication on the 17O-excess parameter. Furthermore, we now better point out the main objectives of the manuscript to: 1) test the potential of triple oxygen isotope analyses to resolve fundamental hydrologic processes of evaporation and mixing of sources that cannot be resolved by the classical δ^2H-δ^{18}O analyses; 2) test the robustness of the Craig-Gordon model in a highly dynamic environment with considerable seasonal variability in all the model input parameters; and 3) demonstrate the potential of triple oxygen isotope analyses to derive the hydrological balance of lakes from water isotope and climate monitoring. The site of the Salar del Huasco was chosen because of its known extreme seasonality in order to obtain a maximum range of isotopic variability as a result of the above processes. The study’s purpose was not to primarily investigate the seasonal dynamics of the Salar del Huasco in detail.

Secondly, the issues with the presentation of the methods and sampling are closely related to the third issue (results and discussion). Some of the information in “Sampling” belongs in “Study Site” (e.g. connectivity of ponds) and the section would benefit from more emphasis on the different conditions of each area during the sampling periods.

We have realized that there has been a doubling of information in the sections of “Study Area” (L81-94) and “Sampling” (L115-129). We complemented the paragraph in “Sampling” with the information given in “Study Area” and removed L81-94.

Through the “Sampling”, “Methods”, and “Craig-Gordon” sections (as well as some introduction parts) there are terms that are not introduced properly or defined (e.g. d-excess, E/I).

All variables in the main text are now defined properly. Furthermore, we added a detailed section on the principal isotope systematics in the supplement, in which all the formulas and variables that were used, are defined, and provided in a table, together with respective references.

The “Sampling” section does not include the measurement height of the atmospheric data that was collected (temperature, relative humidity, δv), which may be significant for use in the Craig-Gordon model.

We added this information.

The section on Craig-Gordon modelling lacked sufficient detail to allow for the replicability of the results. The formulation of the Craig-Gordon model used for oxygen-17 was not provided (I assume it is a similar form to Surma et al., 2018) which would be useful for the readers to understand the sensitivity assessed by the authors. It would also be useful if the authors would provide the other values used in the Craig-Gordon model (e.g 17αl-v_evap, 17αl-v_diff).

Indeed, we had not described the theoretical background of the isotope systematics and the Craig-Gordon model. We added a respective paragraph in the Craig-Gordon section. Details on the fractionation factors that were used are now given in the theoretical section in the supplement.

Additionally, there is no information on how the authors accounted for mixing. Is it changes to the input endmember? Is it changes to the E/I ratio?

There are various forms of mixing. In our case mixing may occurs episodically due to seasonal fluctuations in the groundwater table. When the groundwater table rises in the rainy season isotopically light groundwater is admixed to the evaporated ponds. We account for mixing by simply calculating two component-mass balance. We clarified this in the respective paragraph in the C-G section and added the mass balance equation.

Thirdly, there are three main issues with the results and discussion section, the number of new methods introduced in the results, the amount of significance placed on few data points (vapour compositions), and the limited discussion of the results. Methods introduced in the results section include the HYSPLIT model (results shown without any previous mention of the model), translation ofδ18Op (from OIPC) toδ18Ov, Monte Carlo simulations and fitting of Craig-Gordon to evaporation pan data, and the set-up of sensitivity testing and the evaluation of the sensitivity. These components should all be introduced and described in the methods section.

We have realized that the original manuscript had structural issues. We will follow these suggestions in the revised version of the manuscript as we have realised that it significantly improves the readability of the text and makes key messages clearer.

We added subsections on the determination of the turbulence coefficient, atmospheric vapour and the model sensitivity tests in the methods section. In these subsections, we mainly integrated information that was previously distributed in the study area or results/discussion sections. In the atmospheric vapour section, we now explained why the OIPC model is not suitable at our study site.

Through the results and discussion section, a lot of weight was placed on the atmospheric vapour compositions which were sampled over two days. While these samples are very important to constrain the Craig-Gordon model and an uncertainty approach has been taken to assess some of the variability, the likelihood of large annual variability and impact should be discussed in more detail rather than discrediting the OPIC on two sample days.

We want to make clear that we do not discredit the OIPC model. However, it is highly unlikely that the global OIPC model precipitation database (Bowen et al., 2020) accurately predicts vapour isotopic composition in regions when precipitation events are extremely rare. At the Salar del Huasco, precipitation occurs only seasonally and is generally derived from easterly sources, whereas westerly winds that do not produce precipitation, prevail during most times of the year (Aravena et al., 1999; Garreaud and Aceituno, 2001; Garreaud et al., 2003). We tested if vapour values at the salar are consistent with the prediction from the OIPC model.

We have measured an additional vapor sample that was taken during the field campaign in 03/2019 to strengthen the constraint of the atmospheric vapour value. The dataset remains small, but as pointed out by the reviewer, these data are very important. We also back up the data by verifying the measured vapor composition indirectly from the evaporation experiments. Fitting the C-G model through all experimental data using the measured $\delta^{18}O_V$ value results in a turbulence coefficient of n = 0.5 ± 0.15, which is in good agreement with the global range of reported values.

The discussion of the results is limited, particularly with the model uncertainty and the explanation of the dynamics of the salar, in context to the literature. Some ideas that may help the discussion could include (1) the impact of ice and high temperatures on evaporation pans and isotopic fractionation (2) the larger implications of model uncertainty, and(3) discussion on the causes of intra-annual changes of specific ponds (e.g. causes of shifts in d-excess- or 17O-excess-δ18O space in Figs 9 & 10).

This study focusses on the evaluation of the potential of the triple oxygen isotope system to distinguish hydrological processes of evaporation, recharge and mixing. Resolving intra-annual changes of individual ponds was beyond the scope of this study and requires a more detailed study of the different hydrological subsystems and monitoring at higher resolution. However, we discuss the effect of ice and variable temperatures on the evaporation pans as well as model uncertainty.

If the authors can make substantial improvements to clarifying the objectives and larger significance, describing methods, and expanding the discussion, the results could be a significant contribution for publication. Many of the issues above are described further in the Specific Comments section.

Specific Comments:

Some of the specific comments refer to issues already addressed in the general comments. We will implement changes as stated in the general comments above.

Minor comments regarding typos, rephrasing of sentences or adding of additional information on the sample location and the performance of sampling are all addressed in the revised version of the manuscript.

In the following, we will focus on specific questions that Reviewer #1 raised.

Specific comments related to the general comments:

P1L21-26: What are the results that these tools give us? No need for all of the mineral examples.

P1P26: Change the word “predicts” to a more relevant term

P1L27-29: Sentence not clear

P2L47-58: The section is more of an abstract than an introduction/objectives

The introduction was thoroughly revised.

P1L27: Define α17 and α18

P2L31: Define $\delta^{17}O$ and $\delta^{18}O$

P2L33: Define what “x” is

P2L36: Describe what ^{17}O-excess shows (i.e. more negative is more fractionation/evaporation)

P5L141: d-excess is not defined.

We have added a detailed section on the principal isotope systematics in the supplement, in which all the formulas and variables that were used, are defined properly.

P6L182: Give the method used in Section 6.2 for determining n here

P7L186-191: This should be in the study site section.

P7L194: This should be in methods. How many samples were taken? What was the temporal resolution?

P7L195-199: This should be introduced in the methods section if it is significant enough for a figure in the manuscript. Otherwise, the discussion can refer to it in the supplementary material (with a description of the model in the supplementary material).

P8L235: The description of obtaining $\delta^{18}O_v$ from the OIPC needs to be earlier

These comments refer to restructuring of the manuscript and the addition of subsections in the “Methods”. We have thoroughly revised the structure of the manuscript. We added subsections on atmospheric vapor/OIPC/HYSPLIT and the determination of the turbulence coefficient in the “Methods”.

P7L200: There needs to be a definition for the OIPC.

P7L200: How did you get the $\delta^{18}O_v$ from the precipitation? What values did you use for the correlation of precipitation to vapour? Also, the Bowen et al., 2005 reference should be for monthly values not annual values. Bowen et al., 2003 should be for annual

P10L293-294: “two-spot measurement”. Two measurements? Two-days of measurements? It is not clear how many measurements there are from the methods section.

P7L205-208: Provide references that would suggest that the OIPC would not provide a reasonable annual or seasonal value of precipitation. The OIPC isn’t intended for use on temporal scales less than one month (in an average year), so it would not be surprising if two samples may deviate from the average of a month.

These comments address the issue of estimating the isotopic composition of vapour from the OIPC model or direct measurements. As stated in the ‘General Comments’, we do not want to discredit the OIPC model but we had to test its reliability for our very specific sample site.

P8L218: Why a monte carlo approach? There is only one unknown. There is no previous description of monte carlo simulation approach to the C-G model

P8L218: With the monte carlo approach did you take the best value? Is there no uncertainty with the Monte Carlo approach here?

P8L230: Is the fitting done via a step-wise approach? Needs to be clarified.

P8L230: How much is “considerable sensitivity”?

These comments refer to the determination of the turbulence coefficient. We added a subsection describing the method how to determine the turbulence coefficient in the methods section. We will provide errors for the determined turbulence coefficient estimated from the uncertainty of input parameters. For this purpose, sensitivity tests were performed, which will be provided in the supplement.

P10 L309: where does the assumption of ± 5 ‰ come from? How was this value determined? Is it from the uncertainty of the OIPC? Is it the range of monthly precipitation isotopes?

We will add details on how the uncertainty of individual model parameters was estimated and extend the discussion on model results in the revised manuscript.

Specific questions:

P3L81: Is there water loss from the lakes back to the groundwater system during low groundwater levels?

We think, loss of water from the lake by “infiltration” additionally to evaporation at low groundwater levels is likely, but we do not have evidence for this. However, this would not affect the isotopic composition of the remaining pond water as infiltration should not lead to isotope fractionation.

P4L104: Is the evaporation pan completely thawed at 9:30?

No, it is not. But we do not know the exact time interval, which will also shift a bit depending on the amount of frozen water and the amount of remaining water. Because the exact time interval is unknown, we the period when T > 0°C as the effective time interval. Even if the time interval was delayed, this has only a minor effect on the average temperature and relative humidity values. Furthermore, sensitivity tests demonstrate that even high uncertainty in T and rH have no significant impact the modelled turbulence coefficient.

P5L135: There was no previous mention of chemistry data. This data would be a useful discussion point in the manuscript for water sources and would help justify input sources for the Craig-Gordon model and the overall mixing of salar.

We agree, but this topic is beyond the scope of this manuscript. However, we now mention that the TDS data confirm mixing in plots of $\delta^{18}O$ vs salinity.

P5L141: Why is d-excess reported here when d-excess is dependent on δ18O and δ2H

We are not sure to what this question is referred to. Meteoric waters fall on a trend line, where the slope is mainly defined by equilibrium fractionation during condensation. Kinetic processes, e.g. evaporation progress along shallower slopes. These processes cannot be distinguished by δ18O or δ2H alone. The d-excess parameter quantifies the offset from this slope and thus better visualizes the proportion of different fractionation effects in the $\delta^{2}H$-$\delta^{18}O$ system.

P6L156: “e.g. as a result of flooding or snowmelt”. Meaning the addition of other source waters?

Meaning one event in which e.g. flooding water is mixed into the pond water. In such short-term events the isotopic composition of the pond water may be affected by a mixing process (simple mass balance between two water masses [‘pristine’ floodwater and pre-evaporated pond water]) rather than by a change in recharge conditions. We added a few sentences explaining how we account for these mixing events in the “Craig-Gordon” section (see above).

P6L158: What was used to create Figure 3? There isn’t much discussion of what is on Figure 3.

It's a schematic figure showing that different trajectories for simple evaporation, recharge evaporation, and mixing can be well distinguished in triple oxygen isotope space (A), while they merge in data uncertainty in the plot of d-excess vs. $\delta^{18}O$ (B). The discrimination of these three trajectories is almost independent of the input variables (h, T, n, δ_{WI}, δ_V). The Craig-Gordon equations that were used to model the trajectories for simple and recharge evaporation were added. Furthermore, the paragraph on mixing was extended (see general comments).

P6L167: Oceans have a value of≈0.5, stating a theoretical value doesn't make sense here under natural conditions.

The data from Uemura et al. (2010) imply a turbulence coefficient n = 0.3 (due to sea spray….), but this value is likely biased due to sea spray. Other than that, we are not aware of any published $n < 0.5$, indicating that such conditions are at least rare.

P6L180: What about the diffusive properties? They could have a large effect on the results.

We state that h, T, δ_{WI} and δ_V can be obtained by direct measurement or monitoring, but the turbulence coefficient, which accounts for diffusivity conditions, is not easily obtainable (Line 180 – 182). We accurately quantify the turbulence coefficient from isotopic data of pan evaporation experiments.

P8L220-221: What about changes to evaporation due to the overheating of the evaporation pans?

Good point. Temperature and relative humidity in the C-G equation are related to the evaporating water surface rather than air. Air temperature and water temperature are often assumed to be equal, but we observed temperature differences between air and water of about ± 5°C. However, sensitivity tests with this temperature range show that uncertainty in the actual temperature value have no significant impact on the modelled turbulence coefficient.

P8L225: What about the effect of fractionation due to ice-freezing and thawing or through sublimation?

Indeed, isotope fractionation effects due to freezing biased our first estimate of the turbulence coefficient as discussed in detail in the text. We then use a second estimate that is not affected by ice-freezing.

P9L262: What about the LMWL?

P9L263: It could fall below the GMWL due to precipitation sources. It would be more relevant if this was compared to the LMWL

A large δ^2H-$\delta^{18}O$ dataset of meteoric waters from the Altiplano region suggests that the LMWL in the δ^2H-$\delta^{18}O$ system is similar to the GMWL (Boschetti et al. 2019 and references therein). Such a dataset does not exist for, triple oxygen isotopes, hence there is no determined LMWL for ^{17}O-excess. In figure 8, we used the LMWL in the plot of d-excess vs $\delta^{18}O$, but the GMWL in the plot of ^{17}O-excess vs $\delta^{18}O$.

P9L276-278: Where is the data to support the evaporation theory? What are the tributary values? How much enrichment is observed from the tributaries to the Collacagua River?

We have only measured the isotopic composition of the Collacagua river and cannot constrain the isotopic composition of its tributaries by own measurements. However, Uribe et al. (2015) investigated the isotopic composition of rivers in the Huasco basin. They demonstrated that the isotopic composition of surface water reflects the isotopic composition of precipitation in the source region, which varies with altitude (more depletion in 18O with increasing altitude). "Downstream the waters become enriched (…), because they receive contributions of water recharged at lower altitudes, which are characterized by a more enriched isotopic content than the water coming from higher altitudes, and also due to the effect of evaporation along the riverbed." (Uribe et al., 2015). We will rewrite this paragraph in the revised version of the manuscript and refer to this previous study.

P10L283: Evaporation and groundwater recharge are the only two aspects tested here, so should be the dominant factors. There needs to be a statement on how equal these factors are.

P10L305: E/I was never introduced. Most figures include this as E/I = 0. Is figure 10 not E/I = 1? Where is the trajectory where E/I6= 1?

The recharge evaporation trajectory is modelled in dependence of the E/I ratio. The equations are now provided in the Craig-Gordon section. The position of the measured isotopic composition of ponds on the trajectory gives an indication of the throughflow rate (close to source water = high recharge, close to terminal lake = low recharge, below terminal lake = evaporation exceeds inflow and the lake tends to desiccate).

Section 6.4.2: Suggested that the causes of intra-annual changes (e.g. Figure 10) are discussed for different ponds. E.g. changes in E/I for a given year?

Monitoring at higher resolution and more information on recharge/evaporation rates as well as about the subsurface groundwater regime are required to quantify intra-annual changes in E/I in individual ponds.

Minor comments:

P1L19: Is it really a main finding to give a specific value of wind turbulence?

P1L14: What is "recharge evaporation"

P3L72: How many years were used for long-term averages?

P3L86: Change the word "probably"

P4L98: Suggested change to "...18:00, but on the third day at 13:00".

P4L100: Where are the weather station and evaporation pan? What are the '+' markers in Figure S1? Is that water temperature?

P4L100: take out "at the experiment"

P4L114: Remove "i.e. the general direction of the Pacific coast".

P6L154: Change the wording of "classic evaporation theory".

P6L154: There are more than two scenarios; this manuscript is only examining two.

P6L157: What trajectories?

P6L164: "initial or inflowing water". Should this be "initial and inflowing water"? In general, these two are different components. An assumption needs to be stated here that they are the same.

P6L170: Remove "classic"

P6L175: This is more results using data from the region rather than a method. Each subplot needs to be described or this should be in the supplementary materials.

P6L182: What was the height of the measurement? Is it still used if it may not be representative? Not clear what value was used in the end.

P7L204: "rainfall data", suggest a change to "rainfall isotopic estimates"

P7L213: change the wording of "well constrainable"

P7L214: Suggest changing "...derived empirically from a plot..." to "...estimated from a best fit curve..."

P7L215: Fig 6a

P7L216: What is meant by "barely sensitive"?

P8L217: "this approach" suggest a change to "the C-G model"

P8L234: Is stating the $\delta^{18}O_v$ necessary?

P8L239: Re-word the sentence. Why would it be tentative?

P8L251: Re-word the sentence. "fortunately"? The abstract and methods suggest that this value is well constrained. If it is not sufficiently well constrained, then there should be a suggestion for further analysis and measurements.

P9L265: Fig 8b not 7b

P9L266: Again Fig 8 not 7

P9L267: Again Fig 8 not 7

P9L271: Show the sample location on the site plot

P10L290: "following". Following what?

P10L295: Suggest "estimated" rather than "derived"

P10L295: "Previously shown" shown in this study? Or which studies also show this?

P11L317: Should be "°C" rather than "%"

P11L328: Which ponds are E/I > 0.5?

P12L349: As with the abstract, I would suggest clarifying "recharge evaporation" here. It is defined in the manuscript as an evaporation trajectory of a pond sourced by recharge that has evaporation, but it is not clear unless one line in the manuscript is read.

There are a number of minor comments regarding typos, rephrasing of sentences or simple adding of information on sample location or height of measurements. We will follow these suggestions in the revised version of our manuscript.

Comments on figures:

Figure 1: I would suggest adding in the measurement location of the Collacagua River here

Figure 2: For this figure and other figures, while the colour scheme is good, I would suggest that the symbols be unified for the ponds (e.g. using square for all ponds/lakes and triangles for springs). The upside-down triangle (Laguna Grande) is difficult to identify on some plots).

Figure 3: What values were used to create the conceptual figure?

Figure 4: Is there an expectation of significant evaporation when the temperature is 0°C?

Figure 5: Is this figure necessary for the manuscript. There is a similar figure in the supplementary materials that would suffice. What are the thin lines on the figure?

Figure 6: What is the starting value of each interval?

Figure9: Relabel the figure to make clearer. It is not clear that the left-hand side shows the ^{17}O-excess v. δ^{18}O while the right hand side it d-excess v. δ^{18}O.

We are grateful for the detailed review and these useful suggestions that help to improve the illustration of our data. We will implement these suggestions in the revised version of the manuscript in terms of what we consider as a meaningful improvement of the presentation of our data. We will carefully evaluate which figures should be shown in the main text and which should be included in the supplement.

References:

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