

Reviewer 2 comments (response in red)

The paper “Evidence for high-elevation salar recharge and interbasin groundwater flow in the Western Cordillera of the Peruvian Andes” by Alvarez-Campos presents a multi tracer (isotopic and geochemical) assessment on the influence of groundwater flowpaths from a close basin salar in spring water upwelling at lower elevations that supply water to the city of Arequipa, Peru. Overall, I find the paper well-structured and clearly written and the findings generally well supported by the presented data and analysis. My major concern relates to the insufficient description of sampling collection and laboratory analyses. Given the relevance of the paper for the management of water resources in the region of study, I consider it is suitable for publication in HESS after some points described below are implemented in the manuscript.

We thank the reviewer for highlighting methodological details that were missing and can add them to the manuscript.

Major comments:

L111-113: tritium and residence time come as a surprise for the reader. I suggest adding a few statements or a short paragraph to the introduction mentioning the value of tritium in the context of the study, highlighting particularly research on the study region for similar purposes.

We can add a short paragraph introducing the value of tritium in the context of this study in the revised manuscript.

Section 3.1. It would be helpful to include the elevation of the sites for reference in this section so the reader does not need to check Table 1 many times. Also, it is confusing that the authors sometimes mentioned only the names of the sites, other times only the sites IDs (presented in Table 1), and others, both names and IDs. I strongly suggest to homogenize this in the whole manuscript, figures and tables for consistency and clarity (i.e., this issue is common in this and the rest of the paper sections).

This is a helpful suggestion to improve readability of the manuscript.

L260: describe how snow was sampled.

Detail on snow sampling were added.

L261: report the period and frequency of rainwater sampling. If not collected throughout the whole study period, indicate why. I strongly suggest to give a name to the precipitation water sampling in Table 1 and use it in the whole manuscript. Also, show it and add it to the legend in all relevant maps.

Rain was sampled over the monsoon season January-March. The rest of the year there is no precipitation to sample. We can include this clarification and give it a site ID.

L267-272: the description of water sampling collection is quite incomplete and requires substantial improvement. Some of the main issues are: how was water from river and springs samples? How were samples collected for stable isotope analysis stored to avoid fractionation by evaporation? How was rainwater sampled to assure evaporative fractionation did not affect the water samples? What sites were samples for tritium, specify? Report the make, model, and accuracy of devices used to measure physico-chemical parameters in situ and how often and how they were calibrated. Please update the paragraph with this and other relevant information that might be missing.

We detail in the methods isotope section 3.1 how samples were collected, storages and sealed to avoid evaporation. We have added further details on rainwater collection and evaporation. Samples for tritium are listed now in the methods section. In situ calibration and instrumentation data are included now for the Oakton pH meter and daily sensor calibration in the field.

L286: I am puzzled about the construction of the LMWL using data for 3 months only. In section 2.3, it is mentioned that the very dry winter occurs between June and August, however, it is not clear if precipitation during those months is at all nonexistent, or just very little compared to the wet summer monsoon one (November to April). Even for the latter, using an isotopic dataset from January through March 2019 might not be entirely representative of the local conditions. I strongly suggest the authors to include a time series of precipitation during the study period in the paper for reference, and discuss if and how the limitation of the available isotopic dataset could influence their findings. Showing the precipitation amount data could also help to link their findings about the influence of modern day recharge on their findings and the developed conceptual model.

It only rains a few months out of the year, during the summer (~Dec-Mar). Our 2019 precipitation sampling is effectively an annual summary. For the reviewer's reference, the LMWL calculated for the 2019 wet season was $y = 8.01x + 8.40$. Including 2020 precipitation, the fit was very similar, $y = 8.05x + 10.91$. We would be happy to include the monthly rain amount data to illustrate the seasonal rainfall in this location. However, we do not base any of the conclusions or analysis in the paper on the LMWL. It is only provided for general context. A separate manuscript is submitted that analyzes the daily precipitation water isotope data from an atmospheric process perspective. Adding it here would add unnecessary detail to an already lengthy paper.

Section 3.3: there is very little information about the chemical analysis. Please report standards, calibration curves, detection limits, etc. used for the analysis of anions and cations. Also report QA/QC procedures to secure high quality of the produced data.

These can be added.

L.346-350: I strongly suggest to show the data supporting these statements (i.e., similarity between spring and surface waters). One option is to have a subplot in Figure 6 showing the springs' isotopic compositions. It would also be good to include the isotopic

composition of precipitation in such a plot (e.g., adding a third panel, or plotting together with the springs and surface water isotopic fingerprints?)

L.447 and L.502: how do the authors infer that residence time should be several hundred years old? If anything, based on the Tritium dead results, one could say that groundwater is older than ca. 60 years based on the 1960s bombings. However, without further evidence, saying that water is of certain age seems arbitrary and could be misleading. The authors might be right, but further discussion is needed to justify their statement. Otherwise, please recognize the limitations of the presented dataset and do not speculate about water aging. Based on this comment, I strongly suggest the title of section 5.3 is updated to "Insights into groundwater age" or something similar since results presented are not conclusive.

This is based on recharge-weighted well-mixed aquifer models that were informed using time series from Albero & Panarello (1981) and some back-of-the-envelope calculations of specific discharge. The mixing models have high uncertainty because these models are sensitive to the fraction of recharge that is used to weight the tritium annually. We think that these springs likely have residence times falling between the ranges for tritium and radiocarbon. The flow calculations are uncertain because the region is data poor and we do not have well-constrained hydraulic parameters. Therefore, we will simply state that the groundwaters are older than 60 years until additional data become available.

Light/heavy versus enriched/depleted: throughout the manuscript, the authors use these terms interchangeably. I strongly suggest the authors to avoid using the terms light/er when referring to depleted isotopic compositions to avoid confusion with the commonly used isotopic terminology of light (more abundant) versus heavy (less abundant) isotope ratios. Please revise the whole manuscript to make changes accordingly.

We can make these changes and remove informal usage of light/heavy.

Minor comments:

L50-55: Please support these statements with appropriate references.

L65: add references to support the final statement of the paragraph.

We can add additional references.

L67: this is not true for the whole western South America because i) the northern (tropical) Andes in the north are generally humid and salars are mostly common in areas of the central Andes. Please specify the particular region of the Andes for which this statement applies in the whole manuscript.

We can make this clarification.

L96: report elevations of the Laguna and salar

This information was added

L145-147: add references for the statements in these lines

References can be added.

L159: similar to L67, specify the specific region across the Andes for which this statement applies.

We can make this clarification.

L170: specify which rivers

This information was added

L173: from 2018 to ??? please specify

This sentence was modified to specify that this is annual 2018 precipitation data.

L196: report values of the predicted precipitation decrease

L227-232: Misti and Pichu Picu volcanic complexes are quite relevant for context. It would be super helpful to show them in Figure 3.

We can add labels.

L261: report names (or IDs) of the sampled springs

Sample IDs were added in the text

L.282: add references for memory effect on isotopic analysis

OK

L.290-292: six sampling sites are listed here, whereas only four sites were mentioned in section 3.1. Please clarify. Also, please report the instrument and standards used for tritium analysis

The four sites mentioned correspond to samples analyzed for tritium, which were snow from Pichu Pichu Volcano, springs from Laguna Salinas, one spring from Characato, and one from Chiguata. Section 3.1 indicates that we sampled six springs. Four of these springs obtained in the district of Characato, and two other springs sampled in the district of Chiguata. This refers to low-elevation springs, and this has been clarified in the revised manuscript. Instrument and standards used for tritium analysis were added.

Sections 4.1 and 4.2: I suggest merging both sections into a single one as they present very similar and related information. Suggestion for title of new sections: Isotopic composition of precipitation, surface, springs and salar water (i.e., dismiss the times series portion of the titles)

Section 4.2 was kept separate to avoid confusion with groundwater in section 4.1, but the reviewer makes a good point that precip and salar waters are not groundwater either. We don't mind combining them.

L304: cross-referenced subplot 4c) is missing. See comments in Figure 4 below and update accordingly.

Subplot c was removed from the figure, but not the legend. We will fix this.

L308: cross-referenced subplot 5c) is missing. See comments in Figure 5 below and update accordingly.

Subplot c was removed from the figure, but not the legend. We will fix this.

L.373: briefly justify why the use of the Gibbs diagram could be considered robust for the study area groundwater. According to Marandi and Shand (2018), page 211, "It remains possible that recharging waters cross the water table with a chemical composition plotting in the upper right corner of the Gibbs Diagram, perhaps particularly in regions where land uses have caused salinization of soils or other artificial impacts to near surface mineralogy." We propose that saline water from the salar provides recharge (therefore the

salar surface waters plot in the evaporative enrichment field) and then mix with non-saline groundwater flowpaths in the mountain block. We infer that this mixing results in Chiguata springs plotting as a mixture of evaporative enrichment waters and precipitation dominant waters.

L.379: Precipitation dominance for any of the samples as suggested here and in the last line of Figure 8 caption. Please revise and update accordingly.

The Quenales Forest springs and Pichu Pichu springs are supported by high-elevation recharge from snowmelt and possibly rain. They are not supported by recharge from saline groundwater and therefore do not plot in the evaporative enrichment field. They do, however, plot in the precipitation dominance field which is physically realistic and defensible.

Section 4.3 I find it odd that geochemical information on surface waters is not described in the results section, particularly regarding figures 9 and 10. Please revise the whole section and describe important results regarding surface waters.

The primary purpose of this project was to investigate mountain groundwater processes that support low-elevation springs. We can add a brief discussion of the surface waters in the revision if it does not add too much to the length. The main observation here is that river chemistry is similar to nearby springs in their respective locations. This indicates groundwater discharge is supporting river flow.

L.418: how was it identified that surface waters were not evaporated? Please mention this in results sections and cross-reference a figure or table to support this observation.

We were referring to the wet season laguna salinas surface water presented in Fig 5.

L.430: enhance local evaporation

L.442: both isotopes actually

L.445: Please show the isotopic composition of Laguna Salinas surface water during the dry and rainy season in the figures.

They are.

L.449: add elevation of Tacune mountains

L.478: cross-reference Fig. 6

L.482: relative to surface-

L.508: please cross-reference Fig. 7

L.548: it is

Table 1: assign a code to precipitation sampling site and add it to the table. Also, specify the period of rainwater sampling, it seems it was January-March 2019 according to the text.

Table 2: as in Table 1, please show clearly which sample sites correspond to the Characato and Chiguata districts.

We can do this.

Figure 2: Suggest to use a topographical map instead so that the elevation differences are more easily visualized. Also, it would be very useful for the reader if the area shown in figure 3 would be marked in this map for reference. It would also be very helpful to show

the different water types samples in different colors for reference in the legend of the figure. Also include this in the caption: "Names of the sampling sites are shown in Table 1 for reference".

These are nice suggestions. The other reviewer suggested we include the faults and using different symbols for the types of samples would be helpful. Adding topography might make it too busy though.

Figure 4: subplot c) is missing. Either add the subplot or update the caption of the figure accordingly. Also, please mark the dry season Laguna Salinas surface water samples in a) for reference.

Subplot c was removed from the figure, but not the legend. Will fix this.

Figure 5: the figure has very low quality, please update it to meet publication standards. Subplot c) is missing. Either add the subplot or update the caption of the figure accordingly.

Subplot c was removed from the figure, but not the legend. Will fix this.

Also, please mark the dry season Laguna Salinas surface water samples in a) for reference.

Figure 6: add the IDs of the sampling sites as those are also used in the manuscript.

Good idea.

Figure 10: quality of the Figure seems to be low. Please improve it.

The quality can be improved

Technical issues – all technical issues can be addressed in the revised manuscript

L67: have formed

L74-77: Very long sentence, difficult to understand. Please rewrite.

L75: suggest using the term tracer instead of component here and in the whole manuscript.

L116: study area

L130: the population of the capital city

L144: 6.7 Ma ago?

L217-219: sentence is difficult to read, please rewrite.

L245: odd sentence in caption of Figure 3. Revise.

L256: six smaller high-elevation

L265: ...in Characato was used to collect rainwater. Also, use the same number of decimals as in Table 1.

L286: were obtained

L.345: spring waters instead of springs

Figure 11: I think it is better to keep using the a) and b) type of cross-reference for the subplots for consistency throughout the manuscript, instead of the current top/bottom.

The other reviewer suggested combining this into 1 panel.

References:

Albero, M.C. and Panarello, H.O.: Tritium and stable isotopes in precipitation water in South America, 1981

Marandi, A. and Shand, P.: Groundwater chemistry and the Gibbs Diagram, *Applied Geochemistry*, 97, 209–212, <https://doi.org/10.1016/j.apgeochem.2018.07.009>, 2018.