

Interactive comment on “Estimating glacier and snowmelt contributions to stream flow in a Central Andes catchment in Chile using natural tracers” by M. Rodriguez et al.

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Author Comments

General comments: We appreciate the feedback provided by the three anonymous reviewers, and will strive to address all concerns in a revised version of the manuscript. In the meantime, we would like to point out the following:

This manuscript is intended as a follow up, or companion, to the work published by Ohlanders et al. (2013) in HESS. Many explanations regarding the experimental design, study area, and the like can be found there. However, we understand the need for each

C3994

article to be as self-explanatory as possible, and in the revised version we will strive to provide as much information as possible, with consideration to available space.

Samples were taken manually and automatically. Manual samples were filtrated in field and stored in insulated bags to keep a low temperature in the samples during field-work. In the lab, samples were stored at 5°C. Samples recorded for cation analysis were dropped with nitric acid (10ml acid/1lt sample) to lower pH and ensure a complete dilution thus avoiding possible precipitation of minerals. Automatic samples were filtered in the lab. The automatic samples were collected each 15 days, which sets the upper limit on the time any sample remained unfiltered. Bicarbonate analyses were not carried out in the automatic samples due to the long time between the collection and the filtration. However bicarbonate was measured in manual samples; likewise, charge balances were made in manual samples to ensure the quality of data. The charge balances in automatic samples were estimated using the bicarbonate present in manual samples made in the same day of automatic collector sampling. Our analysis shows that charge balances remain acceptable even if samples were not filtered the same day of collection. Two principal reasons explain this: first, the storage box for the automatic collector was located in a shaded and well ventilated zone in order to avoid heating of the water samples; second, all sample bottles were treated with a small quantity of mineral oil, which avoids any contact between the water and air inside the bottle. In the reviewed manuscript we will further discuss the charge balances and tritration process applied to our samples.

With respect to the statistical treatment of the collected information, we will provide a thoroughly revised methodology section in the revised paper, and follow the suggestions by the reviewers in terms of analyzing the representativeness of the collected data as end-members for hydrograph separation. We believe that by providing a better explanation of our assumptions, we will be able to argue in favor of our proposed method for combining isotopic and solute information.

Uncertainty in our hydrograph separation estimates will be provided, following the sug-

C3995

gestion from one reviewer, in a manner similar to what was presented in Ohlanders et al. (2013).

Lastly, we will revise the focus of the manuscript in order to balance an appropriate explanation of the statistical analysis of the collected data and the interpretation of the underlying physical processes, in a manner that complements, without repeating, what was previously discussed in Ohlanders et al. (2013).

Following, we provide a point-by-point reply to each reviewer's specific comments.

Reviewer 1:

8953,19-21: DifiñAcult to understand this sentence. Rephrase

AC1. We will strive to improve readability in the revised manuscript. A possible reading of the sentence is "A sub-model was performed using the same principles as the MPCA. In this case, only stable water isotope data was used, and the method is referred to as Isotopic Model (IM)".

8954,17: Readers need more information on the study area. How much of the catchment is glacierized? How many glaciers are there? Are they debris-covered? Do you have any information on glacier mass balance? What is the altitudinal range of the catchment? Is there any vegetation? What do you know about soil development and the thickness of the soil layer?

AC2. We will provide further information about the study area, while avoiding excessive repetition with respect to Ohlanders et al., (2013). While mentioning the characteristics of the glacier catchment (Glac-R1), we will mention that this will later be referred to as "glacierized sources", and explain that it represents mostly, but not only, glacier melt.

8954,18: Consensus in the name of the catchment. Here, the catchment is called Juncal at Juncal River basin, whereas in Figure 1 it is called Juncal basin and Juncal River basin

C3996

AC3. We will revise the naming of all relevant locations in the study area, and strive for coherency with Ohlanders et al., (2013).

8955,9: Mention the speciñA annual discharge

AC4. We agree with this comment. Specific discharge and approximate precipitation in form of rain and snow is important information in a paper that aims to quantify snow and glacier melt

8955,25: What about daily ññCuctuations in ions and isotopes? What are the potential biases caused by the time of sampling during the day? Mention when the samples were collected during the day

AC5. In Ohlanders et al., (2013) we show such an analysis for isotopes. We will include a discussion on this subject in the revised version of the manuscript.

8956,16-18: I am skeptical about this late-ññAiltration procedure, since it is a very reactive geology (limestone). If it was a granitic-gneissic geology or if it was a non-glacial river with low suspended sediment concentrations, it would most likely have a negligible inññCfluence on the hydrograph separation modeling, but in this case this assumption needs to be tested and any biases addressed. Do you have any data about the suspended sediment load?

AC6. Suspended sediment loads are measured at regular intervals by DGA at locations downstream from the study area, and we will discuss these data in the revised version of the paper. We did not make additional SSL measurements as part of our campaign. However we took manual samples at concurrent times with the collector in order to understand the effect of sample storage in the collector. We compared automatic samples with manual samples for each solute, obtaining very small differences in solute concentration between the field-filtered and the laboratory-filtered samples. This result leads us to state that sediment load didn't affect our solute concentration results, and that the effect of delayed filtering is negligible for our case study.

C3997

8957,3-5: Have you quantified the post-sampling dissolution by comparing immediately-filtered samples with late-filtered samples collected at the same time? This needs to be explained in detail. What was the result of this comparison and what are the implications?

AC7. As discussed above, we did perform various analysis in order to study the effect of late filtration; these analysis suggest that the effect of the late filtration was small. We will discuss these in the revised version of the manuscript.

8957,5-7: How did you calculate charge balances without measuring bicarbonate and nitrate (8955,26-8956,1)?

AC8. We did measure bicarbonate in all manual samples. Historical data obtained by DGA show very low values for Nitrate, leading us to suggest that its influence over sample charge balance is minimal. Typical values for sulphate, chlorate and nitrate are between 100-450; 5-20 and 0-0.3 mg/l respectively.

8962,1: This is my main concern about this manuscript. The data is poorly presented. Section 4.1 should be rewritten. It would be natural to start by providing the reader with an overview of all the data and time series. Summarize the ionic and isotopic statistics (number of samples, mean or median, max, min values) in a table. Then present the DGA time-series followed by the UChile time-series (and show the similarity between immediately-filtered and late-filtered samples in a figure)

AC9. We agree with the reviewer, and will provide this information in the revised manuscript.

8962,14-15: Discuss whether the apparent isotopic variability is a consequence of the frequency of sampling

AC10. This variability is a consequence of the difference in altitude in contributing snowmelt, which will be mentioned in relation to what was shown in Ohlanders et al. (2013).

C3998

We found that samples were relatively more enriched in early spring, because snowmelt at altitudes around 2000 m.a.s.l. have a $\delta^{18}\text{O}$ of approximately -15‰ (see Figures 6 and 7 in Ohlanders et al. (2013)). We will strive to provide a much more detailed discussion of this topic in the revised version of the paper.

8966,3: How do you know this? Make a reference to the documentation. Is this statement based on satellite imagery?

AC11. Yes, satellite data show that there was little snow after January 1st. This will be mentioned in the revised manuscript.

8967,8: Mention what the ratio from Ragettli and Pellicciotti (2012) is.

AC12. In the period between December and January in the water year 2005-06 the snow- and ice melt contribution estimated by Ragettli and Pellicciotti is 89.1 and 31.5% respectively, but in a drier year like 2008/09 the contribution was 67.5 and 31.5%.

8967,9: Mention what your "prior information" is

AC13. We will discuss more extensively the use of Liu (2014) data in creating our prior distribution. The Ragettli and Pellicciotti (2012) study pertains to the same catchment, but from a time period of different hydrological characteristics.

8973,13-14: As the aim of the study is to estimate "the hydrological role of glaciers ...", then this must be the focus of the Discussion section. In the Discussion section most attention must be given to the temporal and spatial variations in the contribution from glaciers, and the models should receive much less attention except for a discussion of the differences in the results of the various models

AC14. We will shift the focus of the discussion section to follow this suggestion. We will briefly summarize the discussion on the mass balance of glacierized catchments in the area, starting with Chilean and international references that are mentioned in Section 3.6 in the Ohlanders et al. (2013), but also mentioning the latest Chile papers like Ragettli et al. 2014 (Hydr.Proc.).

C3999

We will also to evaluate if the results are reasonable and what they mean for future water availability in the region.

8975,2-9: This should be moved to previous sections. I do not like the somewhat misleading term "glacierized" . Consider changing this term to "bulk glacier meltwater"

AC15. We will follow the suggestion of the reviewer and find a more accurate term to describe water coming from the subcatchment where glacier presence is predominant (see comment above).

Figure 10: Why are the $\delta^{18}O$ split in two on the 15th of December 2011? What happened on that date? Change the time spacing to start at the 1st of each month. The four lower $\delta^{18}O$ are very important to the objective of the manuscript. They should be shown in a separate $\delta^{18}O$ and at a much larger scale

AC16. The splitting of the figures was done following the change in end-members as discussed in section 4.5.1. We will stress this difference and improve on the presentation of the results as suggested by the reviewer.

Reviewer 2:

1. It is very difficult to read this manuscript and evaluate the quality of the work as much of the basic information such as temporal distribution of precipitation and isotopes, sampling dates and the number of water samples from within the catchment, are not given. Many statements are confusing and imprecise. Moreover, many explanations are given in terms of mathematics, rather than physical processes.

AC17. In our revised manuscript we will improve the description of the study site, sampling and analysis methods, and the hydrological implication of our results. However, we believe that our work does present a methodological contribution as well, and we will strive for achieving a balance in the discussion of both aspects.

2. Although they spent much space dealing with methodology, the key methods on how they determined the water sources and further performed hydrograph separation

C4000

based on the PCA, are still unclear.

AC18. We agree with the reviewer in that much can be done to improve the presentation of our data and methods.

3. I doubt the feasibility of the application of the statistical methods. First, the PCA application in determining the water sources implies that the relationships between the solute concentrations of each source (at least) are temporally constant. However, this is not the case at least for snow and glacier meltwater. Authors did not even mention the fractionation process of solutes and the phenomenon of preferential elution in melting snow and glacier. Please see Leivestad and Muniz (1976), Johannessen and Henriksen (1978), Davies et al. (1982) and Goto-Azuma (1998). Second, isotopic processes and isotope concentrations of snow/water are independent of solute transport processes and concentrations. Thus the PCA application which involved both solutes and isotopes (Table 1) lacked physical basis. Please see Zhou et al. (2008a,b; 2014) for isotopic processes of snow/glacier melting.

AC19. In the revised paper we will include more discussion on elution processes and also stress that one of the most important findings of the work in Ohlanders et al. (2013) was that the spatial (altitude) variability in snowpack isotope composition was more important than temporal variability (i.e. elution) in determining the isotopic quality of river flow.

4. It was concluded that soil water is an important source. However, no soil water was sampled at all. They mentioned some spring samples only. I don't think that spring water can be regarded as soil water. Spring water could be of different types of origin.

AC20. It is true that no soil water samples were taken because resource constraints prevented us from digging wells in the floodplain, and that the source of spring water is uncertain. However, the chemical characteristics of spring samples suggest a longer interaction with rock material, and these characteristics are also seen in river water. We will make a stronger case for this link in the revised paper, and search for a different

C4001

term, such as “reacted water” or “baseflow”.

5. Glacier meltwater samples were collected at the outlet of a sub-basin (Fig. 1). I doubt that those samples were entire glacier meltwater samples because glacier generally covers only a small part of a basin. In the case of raining or much snow in the basin, glacier meltwater could only account for a small portion of the entire discharge at the outlet. The discharging process could last for quite a long time after raining, depending on the basin scale. Moreover, only one site is seen for glacier meltwater sampling (Fig. 1). Glacier distribution in the entire catchment is unknown.

AC21. In the revised paper, we will clarify our assumptions regarding the source of these samples, and provide further evidence supporting these assumptions. We will strive for a clearer definition of what we take to be water coming from a subcatchment primarily covered by glacier ice.

6. Analysis is lacking on the hydrological, solute and isotopic processes throughout the manuscript.

AC22. We thank the reviewer assessment and will strive for a more balanced discussion on the methods and processes in the revised version of the paper.

Reviewer 3:

General comments: please refer to our general author comments at the beginning.

Specific comments: Introduction:

The authors mention the advances of using Bayesian approaches in hydrograph separations because they provide a better means to assess statistical and model uncertainty in the results. Yet uncertainty was only marginally addressed in the actual presentation of results (only on page 8972). I would like to see a more thorough analysis and presentation of the uncertainty associated with spatial and temporal variability in the isotopic and constituent concentrations and the various models used for the hydrograph separation.

C4002

AC23. Please see general author discussion above for the reply to this comment.

Study area: Please add information on the percent glacier cover in the Juncal watershed and the spatio-temporal variability of snow in the watershed (e.g. Over what period does the snow melt? Are there areas where snow lasts over the summer?).

AC24. We will improve the revised manuscript with such description.

Page 8956, line 1: Why not use the chemical symbols (e.g. Mg) instead of element names as was done in the previous paragraph?

AC25. Throughout the revised manuscript we will strive to achieve a much larger degree of consistency in the use of chemical symbols, catchment names, acronyms, and the like.

Page 8956, line 10 ff.: I am assuming snow samples were taken along the road to estimate the change in snow isotopic composition with elevation. How was the spatial variability considered in the hydrograph separations? Including an uncertainty analysis that is estimating the effect of spatial variability in isotopic signals on the estimated source water contributions as done by Laudon et al. 2002 (Oxygen 18 fractionation during snowmelt. . ., WRR), Taylor et al. 2002 (How isotopic fractionation of snowmelt affects hydrograph separation, HP), or Dahlke et al. 2013 (Isotopic investigation of runoff generation in. . ., HP).

AC26. We will include a more detailed discussion on elution processes and the influence of spatial variability in the revised manuscript, and also an uncertainty analysis as suggested by reviewer 3.

Page 8958: Why not just used “RMSE” and “bias” instead of “BRB” and “RRRMSE”?

AC27. We will revise the use of acronyms to conform to editorial guidelines and to ensure readability.

Page 8964, lines 3-5. It is unclear whether the DGA data were projected onto the U

C4003

space of the UChile data or vice versa or whether an independent U space was created from both data sets. Was the entire data set used to create the PCA or was the PCA conducted for the different seasons distinguished earlier? I would like to see a table or box-whisker plot summarizing the observed concentrations at the various sampling points incl. the number of samples that were collected.

AC28. The information content analysis was done in a two-step procedure: i) UChile data was projected onto U-space made with DGA data only, and ii) DGA data projected onto U-space made with UChile data only. Our analysis shows that UChile data can explain more variability, and we used this dataset to build our separation models. All UChile data were used to carry out PCA.

We will add a summary of all collected samples, either on a table format or a plot such as that suggested by reviewer 3.

Page 8964, lines 10 ff.: Which elements were contributed most to the PCA among the 6 listed in line 10? Figure 6 does not really indicate which element (e.g. K or Mg) contributed most to the PCA besides the isotope signals. Thus I would suggest adding a biplot or 3D plot of the first two/three principle components as well as the orthonormal principal component coefficients. In addition, the authors should add a pareto diagram showing how much each principal component explains the variance observed in the data.

AC29. We will strive for providing a better representation of the variability explained by the reduced components in the revised manuscript. We thank the reviewer suggestions in this respect.

Page 8965, line 4: Please provide a short description of what the Hooper approach is.

AC30. We will provide this description in the revised manuscript.

Page 8965, line 9: A more quantitative analysis of the residuals for normality is needed to make this statement. Please see my comment on Figure 7 for details.

C4004

AC31. We agree with the reviewer, and will better sustain our assertion on residual normality.

Page 8965, lines 15-17: A 3D plot showing the sample value cloud and first principle components would be more meaningful especially if including the orthonormal principal component coefficients and labels for the various water sources considered in the PCA.

AC32. Sometimes it is difficult to visualize correctly 3D plots depending on the amount of data shown. We will explore different plotting options, and improve upon the first version of the manuscript. If needed, we will provide supplementary online material

Page 8966: Was the MPCA model created for the entire time period for which data was available or for one or many of the seasonal time periods distinguished in Figure 3. Please clarify.

AC33. It was created for the entire time period. We will clarify the time period validity of this model in the revised manuscript

Page 8966, lines 22-23: Were the studies of Ragletti and Pellicotti (2012) and Liu et al. (2004) performed in the same watershed (Juncal)? If not how can the spring and summer data collected in these studies be used as prior information in the Bayesian model?

AC34. The prior distribution may not necessarily depend only on basin processes or in the characteristic of the basin, but also integrate other sources of knowledge about the topic under study. In this sense we believe that the results of Liu et al. (2004) can contribute as a first estimate of how much water pass through the soil and how much water is unreacted water. The prior distribution is only a first estimation of a process and even if it were rather incorrect, it can be modified by the Bayesian updating, as indeed happens in our case study.

Page 8967, lines 2-3: How were glacier and snowmelt sources split into surface and baseflow components? Please specify the methodological approach for this.

C4005

AC35. We considered as a first approximation the results of Ragletti and Pellicotti (2012) where they consider a separation in rain, snow- and glacier melt. However, we didn't consider the rain since its influence is minimal in summer and we incorporate this percentage into the snowmelt in summer. Notwithstanding, the fraction of soil water wasn't studied by Ragletti and Pellicotti (2012). For the purpose of determine a fraction of soil water the results of Liu et al. (2004) were used. Liu et al. (2004) performed the study in an alpine basin and made HS in different ways. The results concern about reacted and unreacted water where used to estimate a fraction of soil water coming from glacier- and snowmelt. We will include this discussion in the reviewed version of the manuscript. However, even this procedure appear as a rough approximation, it can be performed since the posterior distribution will modify the prior distribution.

Page 8967, line 6: What is reacted water? Please define.

AC36. We define reacted water as water that has been in contact with soil material during a significant time period, thus increasing its solutes concentration. Sueker et al., (2000) give a complete description of those terms. Sueker et al., (2000) establish textually: "precipitation water that reaches a stream without interacting with soil or bedrock may be considered 'unreacted' with respect to geochemical process such as ion exchange or mineral weathering, where as infiltrated precipitation water that has acquired solutes while traveling along subsurface flow path may be considered 'reacted'".

Page 8967, lines 12-14: How was the Bayesian model informed using soil water signatures? Please state the data source and prior information build based on the soil water signature.

AC37. The sources signatures were identified using the samples taken in the basin. In the Bayesian model the mean and variance of each source define a possible mean of the river outlet when several fi are run. The spring samples taken in the basin and the water from Navarro stream in autumn were used as an approximation of soil water (Navarro samples where used because in a fieldtrip in April it was seen that water

C4006

coming into the river would do so in the form of exfiltration from the soil). The prior distribution is a multinormal distribution considering the results of Ragletti and Pellicotti (2012) and Liu et al. (2004).

Page 8967, lines 15 ff.: Please support your isotopic model with statistical proof on significant differences observed in the snowmelt, soil water, glacier melt and streamflow isotopic signatures.

AC38. We performed a Student t-test and we found statistical differences between autumn and spring samples at a 95%. We will show this analysis on Juncal outlet and on sources samples and we will improve our explanation of the isotopic model.

Page 8968, lines 4-5: "the amount of poorly and highly soil. . ." Awkward phrasing.

AC39. In the revised manuscript we will streamline the phrasing throughout the text.

Page 8968, line 9: Please specify which "relative contributions" you are quantifying in this final results section. The current wording does not make this aspect clear.

AC40. We mean the contributions from each end-member or source. In the revised manuscript we will clarify these definitions.

Figures and Tables: Figure 4: The various sampling locations are impossible to distinguish. Please consider either combining all water sources into one symbol or change the scale of each piper diagram to zoom into the diagram to allow a better differentiation of the various water sources. Otherwise this plot does not add much value to the study.

AC41. We will improve this figure, either by zooming into the diagrams, adding legends to the diagram itself, or both.

Figure 5: I don't agree with the apparent seasonal difference in the observed δD vs. $\delta^{18}O$ graph shown in Figure 5. If there is indeed a significant difference in the isotope signal between the three seasons then this could be easily proven with a two sample t-

C4007

test for example. All three seasons clearly cluster within the same value range. Please also increase the line width of the dotted line, which is hard to see.

AC42. Although the samples are similarly distributed along the first axis of variability, the second axis does appear to show seasonality, with most apr-sept samples located above the U1 axis. We will improve the figure, and show the t-test results (which do show statistically different distributions) in order to validate our assertion.

Figure 6: It is not clear from the caption or the actual graphs what this figure is supposed to indicate. One can see the RMSE and bias I assume from the MPCA for different elements used in the MPCA. It would be helpful if a more detailed explanation was added to the caption.

AC43. We agree with the reviewer. The figure is supposed to show the fit of each dataset to a U-space built with the other.

Figure 7: In order for the reader to judge whether residuals are i.i.d. and randomly distributed it would be helpful to add trendlines to the point clouds. In addition, the authors could perform the Lillifors test to assess the normality in the residuals.

AC44. This is true. We will follow the reviewer's suggestion on both accounts.

Figure 8: An actual 3-D plot of the first three principal components including the orthonormal principal component coefficients would actually be a better representation of this figure. As in Figure 4 the symbols are nearly indistinguishable and need to be revised.

AC45. We will attempt to better display this information in a 3D plot. Also we will improve the symbol usage.

Figure 9: For which season or time period is data shown in this plot? Please indicate in the figure caption.

AC46. Figure 9 shows all Juncal outlet and sources data selected for hydrograph

C4008

separation. It is the data for the entire water year.

Figure 10: Please add information regarding the data and model source and time period in the caption. Was UChile or DGA data used for this plot? Is the graph showing the entire period for which observations were available? Plots F and G are hard to read since the legend is covering parts of the graph. I would suggest moving the legend into the dark grey shaded area. In addition, instead of showing the separated flow components in units m³/s I would plot percentages since you use percentages in the text and they are easier to interpret for the reader. One could add a second y-axis label on the right side of the graphs showing the percentages while the left graph will state flow rates.

AC47. In the revised version of the paper, we will modify this figure substantially, following the suggestions of reviewers 1 and 3. Showing percentages together with flow rate units in the same plot might be problematic, since the percentages will always add 100, whereas the total flow rate is changing in time. An additional plot may be added instead, in place of the U or rain plots.

Figure 11: See my comment in Figure 10 regarding y-axis label.

AC48. A similar strategy will be attempted here.

Figure 12: Although being a conceptual graph this figure needs a legend that is explaining the various symbols.

AC49. We agree with the reviewer and will modify this figure accordingly.

Minor comments: Page 8952, line 18: Change "season" to "seasons". Page 8952, line 18: Change "primary" to "primarily". Page 8953, line 25: Insert "it" before "is accepted". Page 8954, line 3: Replace "giving" with "providing". Page 8955, line 1: Replace "site" with "side". Page 8968, line 12: Delete "with" before "nearly"> Page 8973, line 1: Replace "respect" with "compared". Figure 10: Please correct "shows" to plural since you are referring in both instances to two plots.

C4009

AC50. We thank the reviewer for these suggestions and will implement where appropriate.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 11, 8949, 2014.

C4010