Hydrology and Earth System Sciences

Open Access

Discussions

Estimating glacier and snowmelt contributions to stream flow in a Central Andes catchment in Chile using natural tracers

M. Rodriguez[1], N. Ohlanders[3], and J. McPhee[1,2]

[1]Department of Civil Engineering, Faculty of Mathematical and Physical Sciences, University of Chile, Santiago, Chile
[2]Advanced Mining Technology Centre (AMTC), Faculty of Mathematical and Physical Sciences, University of Chile, Santiago, Chile
[3]Center of Applied Ecology (CEA), La Reina, Chile

Correspondence to: J. McPhee (jmcphee@ing.uchile.cl)

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

HESSD

11, 8949–8994, 2014

Estimating glacier and snowmelt contributions

M. Rodriguez et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ ► ►|

◄ ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

This paper presents a methodology for hydrograph separation in high elevation watersheds, which aims at identifying individual flow sources such as snow- and ice melt, rainfall and soil water. Daily summer and bi-daily spring water samples from the outlet of the Juncal River were analyzed for all major ions as well as stable water isotopes, $\delta^{18}O$ and δ^2H. Additionally, various water sources such as rain, springs, snow- and glacial melt were sampled throughout the catchment. A principal component analysis (PCA) was performed in order to reduce the dimensionality of the problem. Potential sources were identified in a two-component U space that explains 77 % of variability. Hydrograph separation (HS) was performed through three models: (i) Isotopic model, (ii) Mixing–PCA model, and (iii) Informative–Bayesian model, with very similar results in each case. At the Juncal River outlet, summer flows were composed by at least 50 % of water originating in highly glaciarized headwaters in 2011–2012 (a dry period in the Central Andes). Autumn and winter flows were highly influenced by soil water and affect total annual discharge. Before the high flow season, snow melt accounted for approximately 25 % of streamflow, However during summer, when streamflow was highest, snowmelt contribution was minimal, while glacier melt and soil water were the most important sources.

1 Introduction

Like many semi-arid regions in the world, the extra-tropical region of South America depends on snow and glacier melt from a nearby mountain ridge (in this case the Andes Cordillera) for its water supply. Although it has been well established that under future climate scenarios Andean watersheds should experience significant changes in the amount and timing of seasonal runoff (Casassa et al., 1998; Marengo et al., 2011; Vicuña et al., 2010), the precise nature of these possible changes is still difficult to describe because of large uncertainties pertaining, among other things, the relative

time-varying contribution of snow and glacier melt as well as subsurface sources to river flow (Ragettli et al., 2013). Without this knowledge, most hydrologic models – even those that are physically based – suffer from over-parameterization and can be subject to large predictive errors. In this work, we combine hydrochemical and isotopic

5 information about hydrologic components in a semi-arid, high-elevation, moderately glaciarized Andean watershed in order to discriminate the most likely sources to the observed river hydrograph at different times during a season; our ultimate goal is to inform future modeling exercises in order to better constrain hydrologic predictions under global change scenarios.

10 Hydrograph separation (HS) using natural tracers can be a useful tool to quantify and describe source evolution in order to enhance hydrological conceptual and numerical models. Many hydrograph separations studies have considered chemical tracers (Heppell and Chapman, 2006; Mul et al., 2008), natural isotopes (Liu et al., 2008) or a combination of both (Merot et al., 1995; Meriano et al., 2011; Ladouche et al., 2001).

15 A review of isotopic hydrograph separation was performed by Klaus and McDonnell (2013) wherein they remark on the spatial variability of isotopic signals as well as on the potential for using both stable water isotopes, and not only one, in order to glean deeper insights on the hydrological function of a basin. Many studies have shown the importance of soil water as a source of runoff during a rainfall event (Laudon and Slay-

20 maker, 1997; Ogunkoya and Jenkins, 1993; Tan et al., 2008; Soulsby and Dunn, 2003). Other HS-studies carried out in mountainous sites have noticed the importance of snow and glacier as primary sources generating runoff (Liu et al., 2004; Cable et al., 2011; Hirose and Marshall, 2013).

Notwithstanding these advances, significant uncertainty remains associated to most

25 methods of hydrograph separation, which can be separated in "statistical" and "model" uncertainty. In this case the first can be due by inadequate sampling in remote areas and fractionation for automatic, un-attended sampling during long periods while the model uncertainty stems from the different options of conceptual hydrologic model applied (Moore and Semmens, 2008; Joerin et al., 2002).

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Some effort has been made in the last few years in order to describe better the contribution from snow- and glacier melt to streamflow in Andean basins (Gascoin et al., 2011; Pellicciotti et al., 2008; Ragettli and Pellicciotti, 2012; Peña and Nazarala, 1987). These works show variable glacier contribution depending on climatic factors, with glacier contribution being more relevant in dry years than in wet years due to the diminished influence of the seasonal snowpack on the former. Other studies on source contribution have been carried out in alpine environments (Martinec et al., 1982; Liu et al., 2004) showing the importance of glacier- and snow-melt in runoff generation and the evolution of stream flow. Glacier ice comprise one of the most important water reservoirs in semi-arid regions, and in dry water years it can supply a high percentage of summer runoff. A description of glacier discharge and its importance as a water reservoir can be found in Jansson et al. (2003) and more recently in Baraer et al. (2012). Glacier melt contribution has been studied using different approaches. Hydrologic models have enhanced the understanding of glacier melt and the evolution of its contribution (Hannah and Gurnell, 2001; Verbunt et al., 2003). Usually, studies of glacier mass balance show meteorological and stream flow data (Kaser et al., 2003; Hirabayashi et al., 2010; Yu et al., 2013; Wagnon et al., 1999), information used to describe the glacier evolution during different season and under different climatic patterns. Other studies have directly measured river flow in alpine regions where water is generated primary due to glacier melt (Singh et al., 2006; Mingjie et al., 2013; Hodgkins, 1998).

Despite these efforts, large uncertainties remain with respect to the hydrologic role of glaciers in remote regions, in no small part due to the inadequate observational networks monitoring this specific aspect of the hydrologic cycle (Pellicciotti et al., 2013). Therefore, novel data collection techniques and improved interpretation tools for information of different origin/type can provide useful insights toward process understanding and improved modeling. In this study we aim at discriminating between glacier and seasonal snowpack melt contributions to streamflow in a high elevation semi-arid Andean watershed. Our analysis improves the understanding of the isotopic and chemical

evolution of a typical Andean headwater catchment, and builds upon the work by Oh-landers et al. (2013), who document the contribution of different sources to river flow using isotopic data measured in different sections of the river, in the snowpack, and rainfall. Now we complement that study by incorporating solute data recorded during the same period and applying multiple models to analyze their performance for hy-drograph separation. Specifically, we aim at: (i) comparing the information provided by a long-term water solute dataset, obtained at quarterly intervals and a one-year, high resolution dataset obtained specifically for purposes of this research; (ii) develop a methodology for hydrograph separation in Andean watersheds with emphasis on identifying glacier-related hydrologic sources to flow; and (iii) estimating the glacier-related contributions to annual and seasonal flow in a representative Andean catch-ment, during a dry year.

In this work, we propose three models to analyze the contribution of different sources to river flow. First, hydrograph separation is performed using the basic end-member mixing analysis (EMMA), with a previous step of Principal Component Analysis (PCA) for reducing data dimensionality. This model is named Mixing PCA model (MPCA). Be-cause extreme component sources are successfully identified, this analysis is able to reproduce the stream water chemistry variability (Christophersen and Hooper, 1992) and hydrograph separation is therefore feasible. A sub-model performed using the same principles that MPCA was built only upon stable water isotope data, and here is called Isotopic Model (IM). The IM avoids the use of precipitable (non conservative) ionic tracers and is based only in the variation of δ^{18}O and δD. Valuable information about the hydrological behavior of our study site can be found in the δ^{18}O-δD plot as we remark further. Many isotopic-only HS studies use only deuterium or oxygen as tracers because is accepted that both isotopes provide redundant information (Lyon et al., 2009). However, studying the δ^{18}O-δD plot, we found that each tracer provides complementary, non-redundant information about the relative contribution of different sources throughout the water year, which motivates us to use both datasets for our analysis. Over-determined solutions of the separation problem (Christophersen and

Hooper, 1992) are avoided since both sets of data are condensed in only one vector through PCA. The third model is an Informative–Bayesian model (IBM). The model is able to separate the discharge in several sources giving as a result a probabilistic distribution of the relative contribution of each source. Bayesian models have been used on several types of mixing problems, especially in ecology research settings (Semmens et al., 2009; Parnell et al., 2010), but for hydrological applications fewer examples exist; Cable et al. (2011) documented source contributions on a glacierized basin using a non-informative hierarchical Bayesian model. Our approach incorporates the knowledge acquired in past studies to the model, and updates the probability density functions (pdf) of relative contributions as new data becomes available.

The MPCA and IBM models cannot be applied continuously along the water year because of two factors: precipitation of ionic tracers and ephemeral presence of snow as a source throughout the catchment. Conversely, the Isotopic Model can be applied continuously, and at a lower cost thanks to the decreasing expense of stable isotope laboratory analysis.

2 Study area and available data

2.1 Study area

The Juncal at Juncal River basin is a 256.2 km^2 catchment within the Valparaiso region, located in the Andes of central Chile 60 km northeast from Santiago, Chile's capital city. The climate is semi-arid with cold winters and warm, dry summers. The mean annual temperature in 2011 at the outlet of the catchment was 9.9 °C. Annual precipitation is about 600 mm at an elevation of approx. 3000 m a.s.l. (Dirección Meteorológica de Chile, 2001) and it occurs mainly in solid phase. The geology of the basin in the eastern site is dominated by limestone, calcite, and calcareous sandstone, which are easily weathered, influencing the chemistry of the river and resulting in high concentrations of sulphate and calcium ions. Volcano-sedimentary strata dominate the local lithology

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

in the central and western site of the basin, with an important presence of dacitic, pyroclastic and basaltic rocks. Older sedimentary strata compose the eastern portion of the basin, and in some areas on the northeastern reaches, natural gypsum deposits have been identified and exploited commercially.

2.2 Hydrometeorological data

Streamflow data are available for the "Juncal at Juncal" stream gauge, which is operated by the Chilean Water Agency (*Dirección General de Aguas, DGA*). This station defines our study catchment outlet, and has been active since 1970. Rating curves are updated regularly, and historical monthly flows range between 1.0 and 30.0 m^3 s^{-1}.

Air temperature, radiation and precipitation are measured at two meteorological stations in the vicinity of the basin, namely "Hornitos" and "Riecillos". The former is operated by the Department of Civil Engineering at U. de Chile, and is located in the outlet of the catchment; the latter is operated by DGA and is located approximately 20 km west from the catchment outlet. The latter station is the nearest precipitation station of the Chilean water agency and has a longer period of record of precipitation and air temperature.

2.3 Water isotope and chemical data

DGA has recorded river flow chemical data at the catchment outlet since 1996, reporting instantaneous concentrations of major metals (Cu, Ag, Al, Mg, Ca, etc.), nonmetals (Cl, inorganic N and P, etc.) and some water quality properties like temperature and pH, every three or four months approximately. Between 2011 and 2012, we obtained a series of ad-hoc measurements of water chemical properties including major natural tracers and isotopic composition, aimed specifically at researching the origins of river flow. River water samples were collected at the basin outlet using an automatic water sampler; the sampling frequency varied from two (early spring) to one day (on late spring and early summer), and water samples were analyzed for sulphate, chlorate,

calcium, potassium, magnesium, sodium, silica, delta value of deuterium and oxygen 18 (Barthold et al., 2010). Isotopic data was obtained following the methodology documented by Ohlanders et al. (2013). Several fieldwork campaigns were carried out in order to sample water characteristics in various-sized streams within the basin, as well as in rain and the seasonal snowpack between January 2011 and April 2012 (Fig. 1).

Two rain collectors were set up on the Juncal basin (The first at the Juncal River Outlet and the second near Juncal Norte glacier) while a third was located in a location outside the Juncal catchment, at an elevation of 2099 m a.s.l. These rain collectors were in place at intervals between September 2011 and April 2012, and as such sampled mostly spring and summer precipitation. Snow samples were collected along a nearby mountain road, in order to study the altitudinal gradient in snow isotopic composition in the range 2200–3000 m a.s.l., as reported by Ohlanders et al. (2013). Also, several snow samples were collected at the Juncal River outlet (2200 m a.s.l.) during the winter season of 2011.

2.4   Laboratory analysis

All water samples were filtered on site at the time of collection (except samples from the automatic collector which were filtered at the moment of sample retrieval, approximately every two weeks) using a 0.45 μm nitrocellulose filter (Type HAWP04700). After filtration, water for cation analysis was acidified with nitric acid at 4N to avoid mineral precipitation and was stored in high-density plastic bottles to ensure complete dilution. Samples for anion analysis were preserved at 5 °C in the laboratory. Titration was conducted at the Water Quality Lab at the Civil Engineering Department and at the Geochemistry Lab of the Geology Department, both at the University of Chile. Major cations as well as Si were measured by an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Optima 7300V, HF version) at the Geochemistry Lab at the Geology Department at University of Chile and by an Inductively Coupled Plasma Atomic Absorption Spectrometer (ICP-AES, Perkin Elmer Optima 3000) at the Research Analytical Laboratory at University of Minnesota. Both results were compared to ensure

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

data reliability. Anion concentrations were measured by an ion chromatographer (IC, 861 advanced compact) at the University of Chile and by an ion chromatographer (IC, Dionex model DX-120) at the University of Minnesota. Samples from the automatic collector and manual campaigns were compared to ensure accuracy between on-site, filtered and non-filtered samples. Ionic charge balances were generally less than ±5 %, although for some samples we did observe differences between ±5 and ±10 %. The largest errors were observed for samples from streams with high solute concentrations.

3 Methodology

As described in the previous section, two different sets of solute data are available. One, here named "DGA", contains long-term (since 1996) data obtained quarterly on solutes only at the basin outlet; the other, available only for water year 2011/12, was recorded at the same site but at a much higher temporal resolution, includes stable isotope information and is complemented with spatially distributed observations of water chemical and isotopical properties. We evaluate the usefulness of these two datasets for hydrograph separation purposes by assessing the fit of the observed data projected onto two different 2-D spaces, constructed with the principal component decomposition of each data set. Subsequently, we estimate the relative source contribution to the daily hydrograph by three alternative models, hereby referred to as: (i) Isotopic model, (ii) Mixing-PCA model and (iii) Informative–Bayesian model. We used principal component analysis in order to reduce the dimensionality of the problem preserving most of the observed variability.

3.1 Data comparison and sources

We compared daily data (UChile) against quarterly data (DGA). In this context, data comparison means that we aim to evaluate the information content in each dataset for the purpose of hydrograph separation. In order to achieve this, a Principal Component

Analysis (PCA) was applied on each data set using the same subset of solute concentrations available both in the UChile and DGA data. The data sets were projected onto two 2-D spaces obtained with the dominant eigenvectors from each PCA in order to compare the mixing spaces determined with each data set, using the root mean square error (R_{RRMSE}) and relative bias (B_{RB}) as fit metrics. It was accepted that the best data for hydrograph separation was that for which the fit metrics were minimal. The fit metrics were computed as:

$$B_{RB} = \frac{\sum_{i=1}^{n} (\hat{x}_{ij} - x_{ij})}{\bar{x}_j} \tag{1}$$

$$R_{RRMSE} = \frac{\sqrt{\sum_{i=1}^{n} (\hat{x}_{ij} - x_{ij})^2}}{n \cdot \bar{x}_j} \tag{2}$$

Where, x_{ij} = raw data in milligrams per liter, $\bar{x}_j$ = mean of each solute, $\hat{x}_{ij}$ = solute projection in the U space (space constructed with eigenvectors from PCA) and n = number of samples recorded. The subscript "i" and "j" represent the samples and solutes respectively.

3.2 Hydrograph separation

3.2.1 Mixing–PCA models

Hydrograph separation was performed using a deterministic method based on solute mass and water volume conservation. The first model is MPCA. All samples were projected onto the orthogonal space defined by the eigenvectors from PCA (U space) and *possible* sources were identified among glacier, snow and soil, thereby determining end-member sources to be applied in hydrograph separation. Juncal River outlet and end-members were projected onto the U space and the Euclidean distance between the U and S spaces (the space defined by tracer data) was computed in order to evaluate the data fit onto the former.

In a three-component model, the hydrograph separation equations are expressed as:

$$C_T^A = f_1 \cdot C_1^A + f_2 \cdot C_2^A + f_3 \cdot C_3^A \tag{3}$$

$$C_T^B = f_1 \cdot C_1^B + f_2 \cdot C_2^B + f_3 \cdot C_3^B \tag{4}$$

$$1 = f_1 + f_2 + f_3 \tag{5}$$

$$f_i = Q_i / Q_T \tag{6}$$

Where Q_i = flow from source i, Q_T = streamflow in the outlet of the basin; numerals indicate sources $\{1, 2, 3\}$; superscripts A and B represent generic solutes and f_i is the fraction of discharge coming from source i.

Moreover, by preserving the information provided by δD and δ^{18}O we are able to develop another HS methodology, here referred to as the Isotopic Model. The model still corresponds to a simple mixing equation on two dimensions given by the isotopic-only tracers, but in contrast to other studies, we recognize that both isotopic tracers provide non-redundant information about the evolution of water sources to river flow. By rotating the coordinate system using PCA we are able to infer important hydrologic properties of the system in question; here the dimensionality of the problem is preserved (two tracers), but the rotation clarifies the dynamic behavior of this hydrologic system.

3.2.2 Informative–Bayesian model

The Bayesian framework was established in order to explicitly account for the uncertainty due to measurement errors, model misrepresentation, and parameter estimation by estimating the *probability density function* of each source's contribution to flow. The aim of the framework is to combine information gathered in previous studies with new data as it becomes available in order to continually update and improve the hydrograph separation model. Compared with the deterministic models described above, the Bayesian approach also enables us to estimate uncertainty bounds on the percentage

contribution of each source, and as such provides information useful for characterizing possible weaknesses as well as for guiding data collection strategies for improving the mixing model.

The Bayesian model can be described by Eq. (7).

$$p\left(\boldsymbol{f}_q|\boldsymbol{D}_{\text{Data}}\right) = \frac{p(\boldsymbol{D}_{\text{Data}}|\boldsymbol{f}_q) \cdot p(\boldsymbol{f}_q)}{\sum p(\boldsymbol{D}_{\text{Data}}|\boldsymbol{f}_q) \cdot p(\boldsymbol{f}_q)} \tag{7}$$

The vector $\boldsymbol{f}_q$ contains the source contribution in each component. The subscript q indicates that q proposed vectors must be generated. The probability $p(\boldsymbol{f}_q)$ represents the prior distribution and $p(\boldsymbol{D}_{\text{Data}}|\boldsymbol{f}_q)$ is the likelihood function of observed data given a state of nature ($\boldsymbol{f}_q$). The denominator is a numerical approximation of the marginal probability, necessary for normalizing the posterior probability $p(\boldsymbol{f}_s|\boldsymbol{D}_{\text{Data}})$. A Dirichlet prior distribution, which is a generalization of the Beta distribution (Parnell et al., 2010), was used in order to satisfy mass balance constraints. The parameters of the prior distribution were calculated using the algorithm presented by Minka (2009) after creating a random one-dimensional normal distribution, representing prior knowledge about each source.

$$0 \le \boldsymbol{f}_q \le 1 \tag{8}$$
$$\sum_i f_q^i = 1 \tag{9}$$

The likelihood was assigned as a multivariate normal distribution, whose dimension depends on the number of tracers selected. The proposed mean and variance were established from random values of $\boldsymbol{f}_q$, considering the mean and variances of the sources (Eqs. 10 and 11) since in this study we apply a simple Bayesian model, as opposed to a more complex model such a Hierarchical Bayesian model (see Cable et al., 2011). We used a simple Bayesian model because given the origin of the available data it is difficult for us to assign a well-suited pdf for hyper parameters. Therefore the mean and

Estimating glacier and snowmelt contributions

M. Rodriguez et al.

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

variance of each source in our analysis was directly set from the values measured. We looked for the simplest Bayes approximation in order to make our result as clear and easily reproducible as possible. Fractionation processes were not considered in the analysis, because our data is insufficient to determine the statistical properties of the fractionation of each isotope in all the sources. Fractionation in river water occurs due to contact between the water, atmosphere and soil. The contact between water and the atmosphere generates a continuous isotopic exchange along the river. Moreover, the contact between water and soil is another interface where isotopic fractionation can occur. These processes cannot be studied with our data, and a more detailed sampling should be performed along the river in order to address this issue.

$$\hat{u}_j = \sum_{i=1}^{n} f_q^i \cdot m_j^i \tag{10}$$

$$\hat{\sigma}_j = \sqrt{\sum_{i=1}^{n} f_q^{i2} \cdot (m_j^i)^2} \tag{11}$$

Where m_j^i is the mean of the jth isotope on the ith source.

Because of the complexity of the analytical solution of Eq. (7), we applied a Markov Chain Monte Carlo (MCMC) algorithm in order to find a solution to the Bayesian model. A block wise updating procedure was used in order to find a solution to the Bayesian problem, a generalized multivariate approach of the Metropolis-Hastings Sampling (Steyvers, 2011). The mathematical approach is detailed in Fig. 2 where p is the target density. θ values will form the probability distribution that must be normalized (in our case θ represents the vector containing the fraction of each source, the asterisk designates the proposal and t the step in Fig. 2) and q is the proposal probability. To discriminate if a θ value is selected or not, a comparison between the "α" value and a random "u" value is made.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

4   Results

4.1   Temporal covariation of available data

Juncal at Juncal watershed outlet data is shown in Fig. 3 in order to illustrate the evolution of all natural tracers together. In order to better visualize the variations of anions, cations and discharge, data was centered and scaled. We split the data from the automatic sample collector in three periods according to streamflow evolution. The first period spans from April to October 2011, when flow is stable in time. The second period is from October to December 2011, when spring melt onset occurs and flow increases rapidly. The last period spans from December 2011 to April 2012, after flow has peaked, and decreases towards fall (April) minima. Figure 3 shows stable, high ion concentrations during fall and winter, changing to lower concentrations during summer and spring. Isotopic behavior is more variable in each season, although relatively constant values can be observed in fall and winter. The highest value is rapidly reached in the middle of October, decreasing to a minimum in mid December. After this, a rapidly variable isotopic signal is observed. More details of this behavior can be found in Ohlanders et al. (2013).

4.2   Stream water chemistry

The piper diagram in Fig. 4 shows the chemical composition of samples taken at different sites in the Juncal River valley. Juncal outlet stream samples (Junc-R1) are similar to Navarro Creek (Nava-R1) and Monos de Agua (Mono-R1), which are streams coming from sulphate-calcium facies with high soil influence. Glaciated flow samples (Glac-R1) are less sulfated and more carbonated due to the minimal contact of this water with east-basin type soils. Samples from the western slopes of the valley (West-R1 and R2) are more similar to glacier samples which both are bicarbonate-calcium faces. High sulphate and calcium concentrations originate mainly by interaction between water and the soil matrix. Juncal outlet samples recorded in our study as well as those

recorded historically by DGA are located in the same area on the piper diagram, so additional analysis are shown in order to assess the information content of each dataset for HS purposes.

4.3 Isotopic characterization of water samples

Data is located in different zones in a δD–δ^{18}O plot depending on the season (Fig. 5). The displacement between data and the Global and Chilean meteoric water line is due to the high altitude of the source areas (above 3000 m a.s.l. in the Andean Ridge – for further details the reader is referred to Ohlanders et al. (2013). In fall (April–June) and winter (July–September) data is located over the first eigenvector (enriched in Deuterium and slightly depleted in Oxygen 18 delta values). In spring (October–December), data moves "across" the first eigenvector and concentrates toward more enriched values in both isotopes. In summer (January–March), data is depleted in δ^2H and δ^{18}O values, although it is less organized in the δ^2H–δ^{18}O plot. Clark and Fritz (1997) established that "an increase on fractionation produced between water and soil minerals results in an enrichment on δ^2H and in a depletion on δ^{18}O which are plotted on the meteoric line". Moreover they stated that changes occur on geological time scales, but we observed that autumn season samples follow this pattern whereas spring season samples behave in an opposite fashion. Further, Liu et al. (2004) recognize an enrichment in δ^{18}O in snowmelt as the melting period progresses, which can explain the movement of samples from the autumn season to the spring season location. Although the measurements lie near the detection limit; the sample cannot be said to be random from a direct inspection of Fig. 5, thus we propose that a seasonal pattern can be discerned.

4.4 Dataset information content, number of sources and hydrochemical data

DGA and UChile data sets were compared in order to determine which was more suitable for hydrograph separation. This analysis only included chemical data because

DGA does not record water isotopic characteristics. First, two different U Spaces were built by performing PCA on the DGA historical data and on our one-year high-resolution data. Then, we projected both the raw DGA and UChile data onto each of the generated U spaces, and calculated the Relative Root Mean Square Error (R_{RRMSE}) and Relative Bias (B_{RB}) for each of the four cases. Our analysis shows that the R_{RRMSE} and B_{RB} are lower or relatively constant when projecting both sets of raw data onto the UChile-based U space Fig. 6.

The number of sources needed for reliable hydrograph separation is studied with all the information collected at the Juncal catchment outlet for the water year 2011–2012. Isotope and chemical data is used to perform the analysis, but we neglected solutes that could precipitate, retaining only Cl, SO_4, Na, K, $\delta^{18}O$ and δD. However, two difficulties arise in the mixing problem when several tracers are available and the HS is attempted for the entire year. As more solutes are incorporated into the analysis, more end-members will be necessary to characterize the variations in water characteristics (Barthold et al., 2011), and the mathematical solution for the mixing problem will be more complex. The second issue is that an annual analysis of all data recorded is complicated by the fact that several sources are activated at different times during a hydrologic year, a feature not easily incorporated into a mixing-type analysis. In order to simplify the analysis we split the hydrologic year in three parts (Fig. 6). During the fall and winter seasons (April to October 2011) saturation index analysis strongly indicates the potential for solute precipitation, so no hydrograph separation was attempted in this period.

Summer (December to April 2012) is characterized by minimal presence of snow over the catchment and some rainfall events that fail to be recorded by the observational network but that leave a trace in the isotopic composition of river water (Ohlanders et al., 2013). It is possible for snowfall to occur above 4000 m a.s.l., melting in a few hours or days. Because of the above, a "pure" snow signal is problematic for end-member mixing analysis. Moreover, although snowmelt could remain in the soil through

summer and contribute later to river flow, our data is insufficient to explain fractionation processes in the snowpack, subsurface or on groundwater throughout the season.

PCA was performed on Juncal River outlet data for the spring (SON) and summer (DJF) seasons. In addition, we applied the Hooper approach (Hooper, 2003) in order to identify the number of sources required for hydrograph separation and to evaluate the quality of the mixing space obtained. The eigenvectors and eigenvalues generated by PCA are depicted on Table 1. 2-D residuals plots for potassium, δ^{18}O and δD show as light, non-conclusive trend (Fig. 7) suggesting the need for incorporating a new eigenvector. In general, 2-D Residual plots are very well behaved. The 2-D U space explains 78 % of the observed variability, which means that three sources are required to explain river solute variability. By the "rule of 1" (Hooper, 2003), this space is well constructed because the next eigenvector (third) explains only 12 % of the observed variability: a threshold of 16.7 % should be reached for an eigenvector to be included in the reduced space.

Samples were projected on a 3-D mixing U space built upon the first three eigenvectors. Juncal River outlet samples did not show a strong variation along the $U1$ and $U3$ axes, whereas possible end-members can be seen from glacier melt, east and west creek, snow and rain (Fig. 8). From Fig. 8 it is possible to identify a pattern in snow, rain and glacier snout river samples on the $U1$–$U3$ plane, all with high $U2$ values. The highest $U3$ rain values were sampled in summer (highly isotopically enriched as stated by Ohlanders et al., 2013), but other rainfall events recorded in spring are located closer to the origin in the $U1$–$U3$ plane, near some of the most enriched snow samples from our dataset. The same altitudinal snow gradient shown by Ohlanders et al. (2013) is seen again in the form of U vectors.

4.5 Hydrograph separation

4.5.1 Mixing–PCA model

Snow covered area is negligible throughout the basin during the summer season, and therefore "direct snowmelt" cannot be a source to flow in this period. In order to differentiate between sources with none or substantial soil contact, we assume here that water coming from the western part of the basin is representative of a "snow" (as opposed to glacierized) end-member. In the western part of the catchment the glacier cover is restricted to small shaded locations and snowmelt is arguably the most important water input. Steep slopes allow only small and restricted aquifers in small, elevated valley floors above 3500 m a.s.l., but their effect on the hydrology of this zone can not be assessed with our current database. Soils are also relatively less weatherable in the western portion, because basaltic, dacitic and pyroclastic rocks are predominant in this area. Therefore, we assume that water coming from the western portion of the Juncal River catchment is a mix of shallow subsurface flow, and direct snow melt. Based on these considerations, we performed EMMA on spring season Juncal outlet data (Fig. 9). The results show that glacierized, snow and east-basin samples surround the Juncal outlet data. The hydrograph separation can be seen in Fig. 10. For summer data we switch to a geographically based hydrograph separation considering east and west soil water from creeks and springs, and glacierized headwater flow.

4.5.2 Informative–Bayesian model

A simple Bayesian model was implemented for spring and summer season data (Fig. 10). Prior information was included from the study of Ragettli and Pellicciotti (2012) and Liu et al. (2004). The former considers discharge as a mix of rainfall, glacier melt and snowmelt, but does not evaluate the influence of soil water. Liu et al. (2004) studied high-elevation basins in the US, using chemical tracers, carrying out separations based on surface flow, soil water and base flow end-members, as well as on

reacted and unreacted water. In an attempt to adopt a prior distribution coherent with the sources of the current study we split glacier and snowmelt sources into surface and baseflow components. Since we performed our analysis on spring and summer, both time windows are of interest.

⁵   In spring the catchment is dominated by direct flow from glacier and snowmelt, as well as reacted water. Liu et al. (2004) estimated that reacted water contributed with 61 and 44 % of streamflow of flow for each of their study basins respectively. We take the ratio of the results from Ragettli and Pellicciotti (2012) and the average of these values (53 %) to create our own prior information.

¹⁰   For summer season data, we changed the end-member sources because snow cover is negligible throughout the basin. This led us to assume that soil water should replace the snow signal (i.e. a conceptual model assumption) if we accept that snowmelt should reach the river primarily in the form of subsurface flow.

4.5.3 Isotopic model

¹⁵ Isotopic samples show a characteristic pattern due to activation of different runoff sources throughout the season (Fig. 5). Winter and autumn samples are enriched in δD and depleted in δ^{18}O, and are located above the first eigenvector. In spring (and sometimes in summer), samples move below the first eigenvector. We relate snowmelt and the interaction between water and soil matrix with the aforementioned behaviors in ²⁰ Sect. 4.3. In early autumn the basin is free of snow, therefore, discharge at the Juncal River outlet must be from glacier melt or soil water. However, in the fall season, energy inputs are not high enough for us to expect significant ice melt rates. As verified during fieldwork, springs were the most active source of river flow at this time of the year. On the other hand, samples are more enriched in δD and δ^{18}O in spring. Snow ²⁵ and rain samples are more enriched in δD and δ^{18}O than Juncal River outlet samples. Conversely, glacierized samples are more depleted in δD and δ^{18}O than Juncal River outlet samples.

Based on these observations, we associate glacier-snow contribution to the first eigenvector, while the second eigenvector provides information about water with low and high soil interaction. We did not include the last eigenvector in the HS exercise because of a lack of adequate information to define the amount of poorly and highly soil interacted flows when the sample values in the second eigenvector are highest and lowest, respectively. However, the first eigenvector was used to separate the HS in two sources of interest (glacierized and snow sources in Fig. 11).

4.6   Final results

The relative contributions to streamflow estimated with the Mixing–PCA and Informative–Bayesian models are shown on Table 2. In spring, glacierized areas are the most important sources, with a contribution of over 50 % of Juncal River outlet discharge. Snowmelt contributes with nearly 20 % and the remaining 30 % can be described as soil water. In summer, glacier contribution increases, surpassing 60 % of the seasonal volume. Water inputs from snowmelt are not important and soil water remains constant in its contribution. The results of the isotopic model indicate that the annual contribution of glacierized and snow sources approximate 62 % and 38 % respectively. The relative contribution of snow and glacier melt to soil water cannot be quantified with the data available for this study.

5   Discussion

5.1   Data discussion

In tracer-based hydrograph separation studies it is very important to verify that solutes used as tracers are conservative. We used saturation indexes (SI) to identify non-conservative solutes and to evaluate minerals precipitation in the river. Using the Phreecq computer package (Parkhurst and Appelo, 2013), we studied solute precipitation over anhydrite, calcite, dolomite and gypsum minerals as a function of water

temperature and pH at different locations within the studied catchment. Based on the observed water temperatures, we assumed a constant temperature of 10 °C in the Juncal River outlet, 8 °C for higher elevation sub-catchments and 2 °C for the glacier-originating river. Usually in our data, precipitation of calcite and dolomite occurs during low discharge periods over Junc-R1. Some tributaries of the Juncal River show variable behavior. For example, February DGA samples show a slight mineral precipitation of calcite and dolomite on April 2002, whereas in September 2003 all SI are negative (no precipitation). February 2005 shows again slight calcite precipitation.

Conservative mixing is not guaranteed in the Juncal River throughout the study period. We detected non-conservative behavior in the concentration of calcium, sulphate, carbonate and magnesium, expressed as precipitation of anhydrite and gypsum. Therefore, care must be exercised when performing HS, and we chose to apply this method only during spring and summer seasons, when samples have negative or near zero saturation index values. Given the objective of this research, namely estimating glacier contributions to flow during spring and summer, this decision seems justified and assures a small effect of mineral precipitation on the overall conclusions stemming from our work.

5.2 Selection of space dimension

Samples in Fig. 8 show different U value composition for the same source in different seasons. The pattern suggests that as snow is deposited higher in the basin, its $U3$ values are lower and become more similar to the characteristic of glacier-snout samples. On the other hand, rainfall, which in this basin occurs mostly during summer months, has high $U3$ values. Therefore, $U3$ allows us to infer that precipitation (solid or liquid) coming from summer storms is more enriched and is situated above basin outlet samples in the $U3$ direction. Conversely, wintertime rain/snow show lower values in the $U3$ direction. The importance of this lies in that a more complex HS can be performed. The analysis by Hooper (2003) notes some difficulties in 2-D hydrograph separations. Candidate end-members do not fit the base of the data because all end

members have similar $U3$ base values, but it can be seen that high altitude snow shows lower $U3$ values. Nonetheless, when plotting all the potential end-members in the 3-D space together with the Juncal outlet data, we observe that it is not possible to explain the entire range of variability based on the available end-members. Therefore, we attempt to perform a hydrograph separation by retaining only three end-members, in a two-dimensional U space.

5.3 General discussion on the mixing models

The Mixing–PCA model allows us to visualize trends in the data, but also to distinguish sources. Understanding the relative contribution of sources to river flow, it is possible to enhance conceptual models and better describe factors determining river flow variability. If many end-members have been identified and more than one group can be used to carry out a hydrograph separation, the selection of the best group will depend on the sources that need to be identified, on the Euclidean distance from the raw samples to the projection in the U space (Christophersen and Hooper, 1992) and on how the end members surround the cloud of observed river flow composition points. Since only a limited number of sources were identified in this study, we did not perform any particular method to select them. Nava-R1 were selected over Mono-R1 samples as base flow because it was seen in an autumn field trip that most river water was originating from soils at this time of the year (springs, moraine, etc.). We solve our model using six tracers, eliminating non-conservatives ones based on the previously described SI analysis. With a PCA we performed a 3-source hydrograph separation using all tracers.

The Informative–Bayesian model was applied on the same period as the Mixing–PCA model after performing a principal component analysis. Its main advantage is that it can provide uncertainty estimates on the relative contribution to streamflow from hydrologic sources, as well as an indication on how different data can contribute to diminish this uncertainty. On a practical level, the IB Model, unlike the MPCA model, can find a solution to the mixing problem even if there are streamflow samples lying outside the space defined by the end-members: the Monte Carlo sampling algorithm is

Full Screen / Esc

able to approximate these samples, but the modeled values will always lay within the end-member region. The acceptance of these solutions will depend on parameters "u" and "α" (see Fig. 2).

Figure 12 depicts a typical 2-dimensional space in a hydrograph separation model. In a Mixing–PCA model, point B will have a higher contribution from source 3 and a lower contribution from the other sources. But point A cannot be described for a set of f_i, and must therefore be projected onto the line that links sources 2 and 3. The Bayesian model searches the solution for f_i in a different fashion. Point A does not need to be projected to the edge of the cloud of points. The governing equations in the Bayesian approach are the same as for the Mixing–PCA model (Eqs. 3, 4 and 5), so the search for the solution will be carried out inside the triangle defined by the end-members. However, the solution won't be exact, since a set of f_i capable of reproducing the value A in terms of the three end members does not exist. Accordingly, probabilistic estimates of source contribution approaching zero must be studied carefully, because of the possibility of obtaining a feasible but biased solution due to the impossibility of representing the river sample by the candidate set of weights or fractions.

The Bayesian model is capable of finding a solution for multiple sources (f_i, $i = \{1, 2, \ldots, n\}$) in a reduced space. The points around "D" in Fig. 12 indicate the sampling using MCMC. This sample can be obtained with many sources maintaining the constraints given by Eqs. (8) and (9). The acceptance of the candidate solution will be determined by a probabilistic parameter. In the case of the Mixing–PCA model, this cannot be achieved because the problem is under-determined, and many solutions are feasible. On the other hand, if the problem is over-determined with many tracers, the Bayesian approach is capable to find an approximation, unlike the Mixing–PCA model. However, a Bayesian approach is capable of finding an approximation. The error will be given by the distance between the river outlet sample in the tracer space (S space) and the geometrical space constructed with the end-members. It is probable that many feasible solutions will be rejected in the latter case, and the solution will be biased. Rather than running the model without any consideration about the cloud of points and

the geometrical space constructed with end-members, it is appropriate to visualize the problem in order to avoid a biased and out-of-bounds solution.

The isotopic model only uses δD and δ^{18}O as tracers, which allows us to use this model throughout the hydrologic year. The model is based on the assumption that water is affected by isotopic fractionation produced by two factors: (i) interaction with rock at low temperatures and (ii) between liquid and solid water phase.

The first idea stems from the notion that "fractionation between rock and water results in an enrichment of δ^2H and a depletion of δ^{18}O" (Clark and Fritz, 1997). However, two conditions are necessary to observe such fractionation, (i) an important rock reservoir with very low water-rock ratios and (ii) geological time scales, because of very low rates of exchange between water and rock. Enrichment factors of ε^{18}O of 27‰ and ε^2H of −60‰ have been reported by Clark and Fritz (1997). Variations over isotopic concentration in our data are very low between seasons in comparison to those values. Many springs in the basin are present during the entire dry season, and it is therefore probable that water interacts with soil for some months. However, the changes account for only 5‰ in δ^2H and for 1.5‰ in δ^{18}O. The standard error of the analysis accounts for 1.3 and 0.2‰ in δ^2H and δ^{18}O respectively. Hence Juncal River outlet isotopic change between seasons is near the error margin. Our assumption is that water interacts with rock for a short period, sufficient to be modified by fractionation. However, this assumption must be verified with further research.

The second idea that justifies our model is supported by findings by Liu et al. (2004), who recognized that snowmelt changes its isotopic composition during the season resulting in an enrichment of δ^{18}O due to a depletion of δ^{18}O in the liquid water because of fractionation between liquid and solid phases. DeWalle and Rango (2008) show δ^{18}O value increases in all cases during the melt season. A similar behavior has been observed in the stream flow in Alaska during snowmelt (Cooper, 1998).

We associate the first eigenvector with variation between glacier and low altitude snow because "glacier" samples (this is, water samples obtained in the river at the glacier snout) turned out to be the most depleted and show the lowest $U1$ (first

eigenvector) values, whereas snow samples were more enriched respect to the basin outlet data, and showed the highest $U1$ values. The second eigenvector, which may be interpreted to describe reacted water, also displays interesting feature variations in time. In fall and winter, samples are depleted in $\delta^{18}O$ and relatively enriched in δD,
5 just as happens when water interacts with the soil matrix and fractionation is the main isotopic process. Spring samples show the opposite pattern, associated mainly to enriched snowmelt due to isotopic fractionation within the snowpack produced by high melt rates. However, the information available isn't sufficient to perform hydrograph separation in the second eigenvector due to the fact that extreme values in the second
10 eigenvector don't represent absolute values in the amount of reacted and unreacted water.

6   Conclusions

This study documents a hydrograph separation exercise aimed at estimating the hydrological role of glaciers in a high elevation, Andean watershed in Central Chile during
15 a dry water year (2011/12). Water isotopic and chemical characteristics were sampled at high temporal resolution at the basin outlet, and these observations were complemented with information from several locations within the basin, each representing a distinct hydrological feature. Long-term water quality data recorded by the Chilean Water Directorate were assessed in terms of its potential to inform tracer-based hydro-
20 graph separation studies. This first analysis showed that water quality data recorded in a short-term experimental design is richer, if not overwhelmingly so, than long-term information, providing a better base from which extract end-member sources in a rapidly changing hydrologic system. Although not evaluated here, the relatively modest discrepancies in fit statistics between reduced spaces obtained with short and long-term
25 data suggest that small adjustments in the experimental design of operational water quality data retrievals could increase their value for hydrologic research objectives.

This research also demonstrated the capability of combined isotopic and solute information for informing mixing models for hydrologic research in mountain environments. Because of the temporal variability of snow cover, we propose different models for different times of the year, with emphasis on spring and summer months, when the watershed is highly "active", hydrologically speaking. We were successful in reducing the dimensionality of the problem by rotating the system of reference and reducing the variation space to at most three directions, using principal component analysis. A Bayesian version of a mixing model provided uncertainty bounds on the relative importance of each source, and it was found that collected data from the 2011/12 water year narrowed the expected error of our estimates from that expected from the prior estimates based on recent literature. Based on our end-member source analysis, we were able to identify different sources for spring and summer seasons: direct-snow, soil-influenced and glaciarized (i.e., associated with a highly glaciated subcatchment) sources could be identified during spring (September–December), whereas glaciarized and east/west soil sources were identified for summer, when snow has disappeared from the basin.

During 2011/12, the Juncal river watershed experienced very dry conditions, with annual flow on the 8th decile and with winter precipitation having a probability of exceedance of 83 % measured at the Riecillos rain gage. For these conditions, both the EMMA and the Bayesian models yield very similar estimates of source contribution, with glaciarized sources contributing as much as 51–55 % of the seasonal flow in spring. Snow direct runoff accounted for 19–25 % of seasonal flow during the same season, and subsurface sources contributed 20–30 % to spring flow. During summer, the contribution from glaciarized sources increased to 58–66 % of seasonal flow, with the remaining runoff coming from subsurface sources. At the annual level, the isotopic model estimation was that 62 and 38 % of flow could be associated with glacial and snow sources, respectively. This result must be interpreted with care, because the available data is insufficient for estimating the interaction of glacier and snow melt with subsurface reservoirs at an annual aggregation level.

Further research is required to refine this methodology and to incorporate results such as those presented here in hydrologic modeling exercises. Here, were use the term "glaciarized" to refer to water coming from the outlet of a small sub-basin covered by glaciers in more that 60 % of its surface area. However, this term does contain the signal of snow accumulated over the glacier and in the adjacent slopes. Future field designs should sample directly the ice surface, in order to obtain isotopic characteristics associated with superficial ice-cores. Also, the altitudinal variation in isotopic snow properties was sampled at a rather limited range, and higher elevation snow properties may suggest different interpretation of isotopic flow characteristics. Finally, we were unable to obtain direct samples of subsurface water. Future experiments should consider wells dug in valley bottoms, which would allow for an integrated view of the subsurface behavior of relevant aquifer systems in mountain catchments, in terms of isotopic, chemical and hydrologic variables.

References

Baraer, M., Mark, B., McKenzie, J., Condom, T., Bury, J., Huh, K.-I., Portocarrero, C., Gomez, J., and Rathay, S.: Glacier recession and water resources in Peru's Cordillera Blanca, J. Glaciol., 58, 134–150, doi:10.3189/2012JoG11J186, 2012.

Barthold, F. K., Wu, J., Vaché, K. B., Schneider, K., Frede, H.-G., and Breuer, L.: Identification of geographic runoff sources in a data sparse region: hydrological processes and the limitations of tracer-based approaches, Hydrol. Process., 24, 2313–2327, doi:10.1002/hyp.7678, 2010.

Barthold, F. K., Tyralla, C., Schneider, K., Vaché, K. B., Frede, H.-G., and Breuer, L.: How many tracers do we need for end member mixing analysis (EMMA)? A sensitivity analysis, Water Resour. Res., 47, W08519, doi:10.1029/2011WR010604, 2011.

Cable, J., Ogle, K., and Williams, D.: Contribution of glacier meltwater to streamflow in the Wind River Range, Wyoming, inferred via a Bayesian mixing model applied to isotopic measurements, Hydrol. Process., 25, 2228–2236, doi:10.1002/hyp.7982, 2011.

Casassa, G., Espizua, L. E., Francou, B., Ribstein, P., Ames, A., and Alean, J.: Glaciers in South America, in: Into the Second Century of Worldwide Glacier Monitoring: Prospects and Strategies, edited by: Haeberli, W., Hoelzle, M., and Suter, S., United Nations Publications, Paris, 125–146, 1998.

Christophersen, N. and Hooper, R. P.: Multivariate analysis of stream water chemical data: the use of principal components analysis for the end-member mixing problem, Water Resour. Res., 28, 99–107, 1992.

Clark, I. and Fritz, P.: Environmental Isotopes in Hydrogeology, 2nd Edn., Lewis Publishers, New York, USA, 1997.

Cooper, L.: Isotopic Fractionation in snow cover, in: Isotope Tracers in Catchment Hydrology, edited by: Kendall, C. and McDonnell, J. J., Amsterdam, 119–136, Elsevier, 1998.

DeWalle, D. and Rango, A.: Principles of Snow Hydrology, Cambridge University Press, New York, 2008.

Dirección Meteorológica de Chile Publications: Climatologí a regional, Dep. Climatol. y Meteorol., 1–46, available at: http://www.meteochile.gob.cl/climatologia.php (last access: 20 June 2013), 2001.

Gascoin, S., Kinnard, C., Ponce, R., Lhermitte, S., MacDonell, S., and Rabatel, A.: Glacier contribution to streamflow in two headwaters of the Huasco River, Dry Andes of Chile, The Cryosphere, 5, 1099–1113, doi:10.5194/tc-5-1099-2011, 2011.

Hannah, D. M. and Gurnell, A. M.: A conceptual, linear reservoir runoff model to investigate melt season changes in cirque glacier hydrology, J. Hydrol., 246, 123–141, doi:10.1016/S0022-1694(01)00364-X, 2001.

Heppell, C. M. and Chapman, A. S.: Analysis of a two-component hydrograph separation model to predict herbicide runoff in drained soils, Agr. Water Manag., 79, 177–207, doi:10.1016/j.agwat.2005.02.008, 2006.

Hirabayashi, Y., Döll, P., and Kanae, S.: Global-scale modeling of glacier mass balances for water resources assessments: glacier mass changes between 1948 and 2006, J. Hydrol., 390, 245–256, doi:10.1016/j.jhydrol.2010.07.001, 2010.

Hirose, J. M. R. and Marshall, S. J.: Glacier meltwater contributions and glaciometeorological regime of the Illecillewaet River Basin, British Columbia, Canada, Atmos. Ocean, 51, 416–435, doi:10.1080/07055900.2013.791614, 2013.

Hodgkins, R.: Glacier hydrology in svalbard, norwegian high arctic, Quaternary Sci. Rev., 16, 957–973, 1997.

Hooper, R. P.: Diagnostic tools for mixing models of stream water chemistry, Water Resour. Res., 39, 1–13, doi:10.1029/2002WR001528, 2003.

Jansson, P., Hock, R., and Schneider, T.: The concept of glacier storage: a review, J. Hydrol., 282, 116–129, doi:10.1016/S0022-1694(03)00258-0, 2003.

Joerin, C., Beven, K. J., Iorgulescu, I., and Musy, A.: Uncertainty in hydrograph separations based on geochemical mixing models, J. Hydrol., 255, 90–106, 2002.

Kaser, G., Juen, I., Georges, C., Gómez, J., and Tamayo, W.: The impact of glaciers on the runoff and the reconstruction of mass balance history from hydrological data in the tropical Cordillera Blanca, Perú, J. Hydrol., 282, 130–144, doi:10.1016/S0022-1694(03)00259-2, 2003.

Klaus, J. and McDonnell, J. J.: Hydrograph separation using stable isotopes: review and evaluation, J. Hydrol., 505, 47–64, doi:10.1016/j.jhydrol.2013.09.006, 2013.

Ladouche, B., Probst, A., Viville, D., Idir, S., Baqué, D., Loubet, M., Probst, J.-L., and Bariac, T.: Hydrograph separation using isotopic, chemical and hydrological approaches (Strengbach catchment, France), J. Hydrol., 242, 255–274, doi:10.1016/S0022-1694(00)00391-7, 2001.

Laudon, H. and Slaymaker, O.: Hydrograph separation using stable isotopes, silica and electrical conductivity: an alpine example, J. Hydrol., 201, 82–101, doi:10.1016/S0022-1694(97)00030-9, 1997.

Liu, F., Williams, M. W., and Caine, N.: Source waters and flow paths in an alpine catchment, Colorado Front Range, United States, Water Resour. Res., 40, 1–16, doi:10.1029/2004WR003076, 2004.

Liu, Y., Fan, N., An, S., Bai, X., Liu, F., Xu, Z., Wang, Z., and Liu, S.: Characteristics of water isotopes and hydrograph separation during the wet season in the Heishui River, China, J. Hydrol., 353, 314–321, doi:10.1016/j.jhydrol.2008.02.017, 2008.

Lyon, S. W., Desilets, S. L. E., and Troch, P. A.: A tale of two isotopes?: differences in hydrograph separation for a runoff event when using δD versus δ^{18}O, 23, 2095–2101, doi:10.1002/hyp, 2009.

Marengo, J. A., Pabón, J. D., Díaz, A., Rosas, G., Ávalos, G., Montealegre, E., Villacis, M., Solman, S., and Rojas, M.: Climate change?: evidence and future scenarios for the Andean Region, in: Climate Change and Biodiversity in the Tropical Andes, edited by: Herzog, S. K., Martiìnez, R., Jørgensen, P. M., and Tiessen, H., Inter-American Institute for Global Change Research (IAI) and Scientific Committee on Problems of the Environment (SCOPE), 110–127, 2011.

Martinec, J., Oeschger, H., Schotterer, U., and Siegenthaler, U.: Snowmelt and groundwater storage in an Alpine basin, in: Exeter Symposium, IAHS Publ., Exeter, 169–176, 1982.

Meriano, M., Howard, K. W. F., and Eyles, N.: The role of midsummer urban aquifer recharge in stormflow generation using isotopic and chemical hydrograph separation techniques, J. Hydrol., 396, 82–93, doi:10.1016/j.jhydrol.2010.10.041, 2011.

Merot, P., Durand, P., and Morisson, C.: Four-component hydrograph separation using isotopic and chemical determinations in an agricultural catchment in western France, Phys. Chem. Earth, 20, 415–425, doi:10.1016/0079-1946(95)00055-0, 1995.

Mingjie, G., Tianding, H., Baisheng, Y., and Keqin, J.: Characteristics of melt water discharge in the Glacier No. 1 basin, headwater of Urumqi River, J. Hydrol., 489, 180–188, doi:10.1016/j.jhydrol.2013.03.013, 2013.

Minka, T. P.: Estimating a Dirichlet distribution, Ann. Phys.-New York, 2000, 1–13, 2000.

Moore, J. W. and Semmens, B. X.: Incorporating uncertainty and prior information into stable isotope mixing models., Ecol. Lett., 11, 470–80, doi:10.1111/j.1461-0248.2008.01163.x, 2008.

Mul, M., Mutiibwa, R., Uhlenbrook, S., and Savenije, H.: Hydrograph separation using hydrochemical tracers in the Makanya catchment, Tanzania, Phys. Chem. Earth, 33, 151–156, doi:10.1016/j.pce.2007.04.015, 2008.

Ogunkoya, O. and Jenkins, A.: Analysis of storm hydrograph and flow pathway using a three-component hydrograph separation model, J. Hydrol., 142, 71–88, 1993.

Ohlanders, N., Rodriguez, M., and McPhee, J.: Stable water isotope variation in a Central Andean watershed dominated by glacier and snowmelt, Hydrol. Earth Syst. Sci., 17, 1035–1050, doi:10.5194/hess-17-1035-2013, 2013.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Parkhurst, D. L. and Appelo, C. A. J.: Description of input and examples for PHREEQC version 3-A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, in: Techniques and Methods, Book 6, Chap. A43, US Geological Survey, 497 pp., available at: http://pubs.usgs.gov/tm/06/a43/, 2013.

Parnell, A. C., Inger, R., Bearhop, S., and Jackson, A. L.: Source partitioning using stable isotopes: coping with too much variation., PLoS One, 5, e9672, doi:10.1371/journal.pone.0009672, 2010.

Pellicciotti, F., Helbing, J., Rivera, A., Favier, V., Corripio, J., Araos, J., Sicart, J.-E., and Carenzo, M.: A study of the energy balance and melt regime on Juncal Norte Glacier, semi-arid Andes of central Chile, using melt models of different complexity, Hydrol. Process., 22, 3980–3997, doi:10.1002/hyp.7085, 2008.

Pellicciotti, F., Ragettli, S., Carenzo, M., and McPhee, J.: Changes of glaciers in the Andes of Chile and priorities for future work, Sci. Total Environ., doi:10.1016/j.scitotenv.2013.10.055, in press, 2013.

Peña, H. and Nazarala, B.: Snowmelt-runoff simulation model of a central Chile Andean basin with relevant orographic effect, in: Large Scale Effects of Seasonal Snow Cover, Vol. 166, edited by: Goodison, B. E., Barry, R. G., and Dozier, J., IAHS Publ., Vancouver, Canada, 161–172, 1987.

Ragettli, S. and Pellicciotti, F.: Calibration of a physically based, spatially distributed hydrological model in a glacierized basin: on the use of knowledge from glaciometeorological processes to constrain model parameters, Water Resour. Res., 48, W03509, doi:10.1029/2011WR010559, 2012.

Semmens, B. X., Ward, E. J., Moore, J. W., and Darimont, C. T.: Quantifying inter- and intra-population niche variability using hierarchical bayesian stable isotope mixing models, PLoS One, 4, e6187, doi:10.1371/journal.pone.0006187, 2009.

Singh, P., Haritashya, U. K., Kumar, N., and Singh, Y.: Hydrological characteristics of the Gangotri Glacier, central Himalayas, India, J. Hydrol., 327, 55–67, doi:10.1016/j.jhydrol.2005.11.060, 2006.

Soulsby, C. and Dunn, S. M.: Towards integrating tracer studies in conceptual rainfall-runoff models: recent insights from a sub-arctic catchment in the Cairngorm Mountains, Scotland, Hydrol. Process., 17, 403–416, doi:10.1002/hyp.1132, 2003.

Steyvers, M.: Computational Statistics with Matlab, Lecture, University of California Irvine, Irvine, CA, USA, 2011.

Tan, Z., Lu, B., and Wang, J.: Hydrograph Separations Based on Isotopicchemical Mixing Models, in: Advances in Water Resources and Hydraulic Engineering, 231–235, Springer, Berlin Heidelberg, 2009.

Verbunt, M., Gurtz, J., Jasper, K., Lang, H., Warmerdam, P., and Zappa, M.: The hydrological role of snow and glaciers in alpine river basins and their distributed modeling, J. Hydrol., 282, 36–55, doi:10.1016/S0022-1694(03)00251-8, 2003.

Vicuña, S., Garreaud, R. D., and McPhee, J.: Climate change impacts on the hydrology of a snowmelt driven basin in semiarid Chile, Clim. Change, 105, 469–488, doi:10.1007/s10584-010-9888-4, 2010.

Wagnon, P., Ribstein, P., Kaser, G., and Berton, P.: Energy balance and runoff seasonality of a Bolivian glacier, Global Planet. Change, 22, 49–58, doi:10.1016/S0921-8181(99)00025-9, 1999.

Yu, W., Yao, T., Kang, S., Pu, J., Yang, W., Gao, T., Zhao, H., Zhou, H., Li, S., Wang, W., and Ma, L.: Different region climate regimes and topography affect the changes in area and mass balance of glaciers on the north and south slopes of the same glacierized massif (the West Nyainqentanglha Range, Tibetan Plateau), J. Hydrol., 495, 64–73, doi:10.1016/j.jhydrol.2013.04.034, 2013.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Summary of PCA results.

	First	Second	Third
Eigenvalue	52 %	26 %	12 %
Cl^-	0.51	−0.01	−0.41
SO_4^-	0.12	−0.73	−0.11
Na^+	0.50	−0.15	−0.43
K^+	−0.23	−0.65	0.23
δD	0.44	−0.08	0.63
$\delta^{18}O$	0.48	0.12	0.44

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 2. Summary of relative source contribution estimation.

	Spring			Summer		
Model	Glacier	Directly Snow	Soil	Glacier	Soil west (Snow interacted by soil)	Soil east
Mixing–PCA model	55 %	25 %	20 %	66 %	9 %	25 %
Informative–Bayesian model	51 %	19 %	30 %	58 %	16 %	26 %
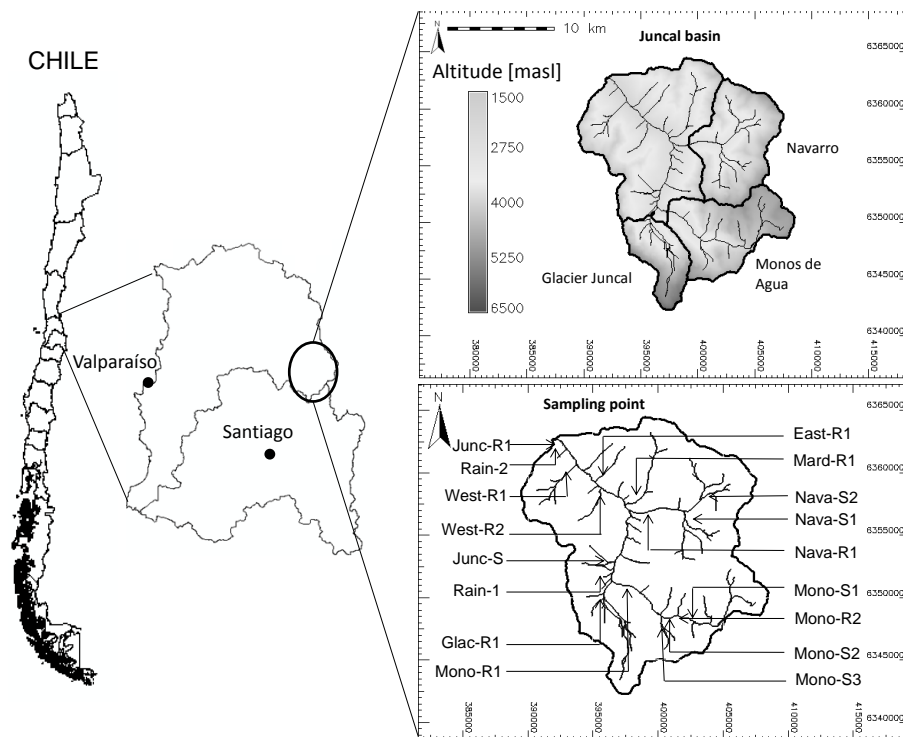
Figure 1. Study Site. Elevation map, sub-catchments and sampling points on the Juncal River Basin are depicted. Our samples are on creek (West-R1, West-R2, East-R1), river (Junc-R1, Glac-R1, Mono-R1, Mono-R2, Nava-R1, Mard-R1), spring (Junc-S, Mono-S1, Mono-S2, Mono-S3, Nava-S1, Nava-S2), rain (Rain-1, Rain-2) and snow (not in the map).

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
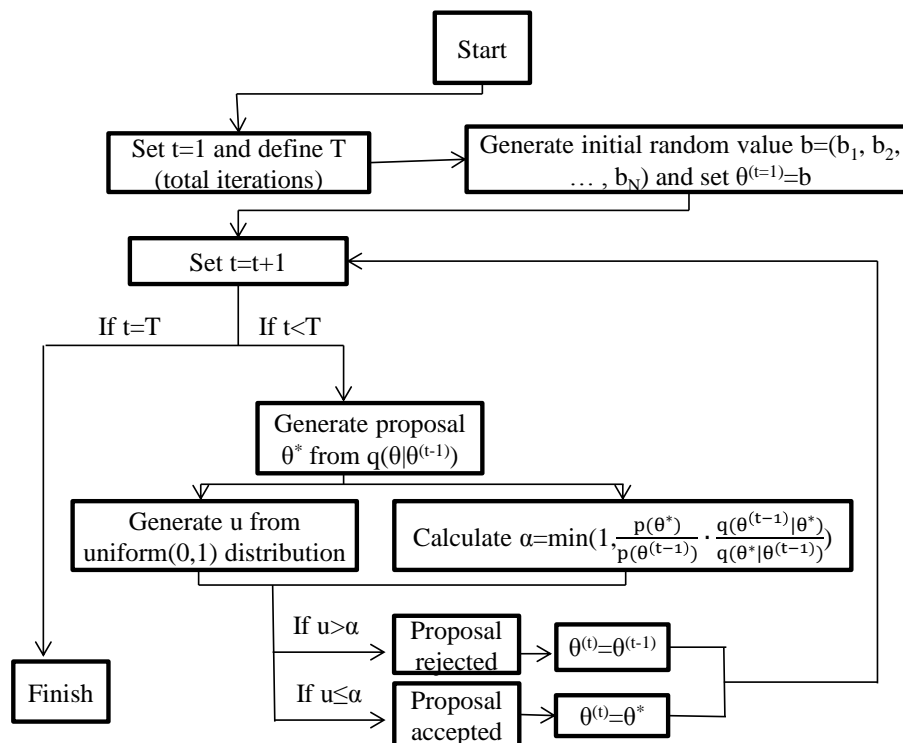
Figure 2. Sampling using Metropolis-Hastings approach.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |
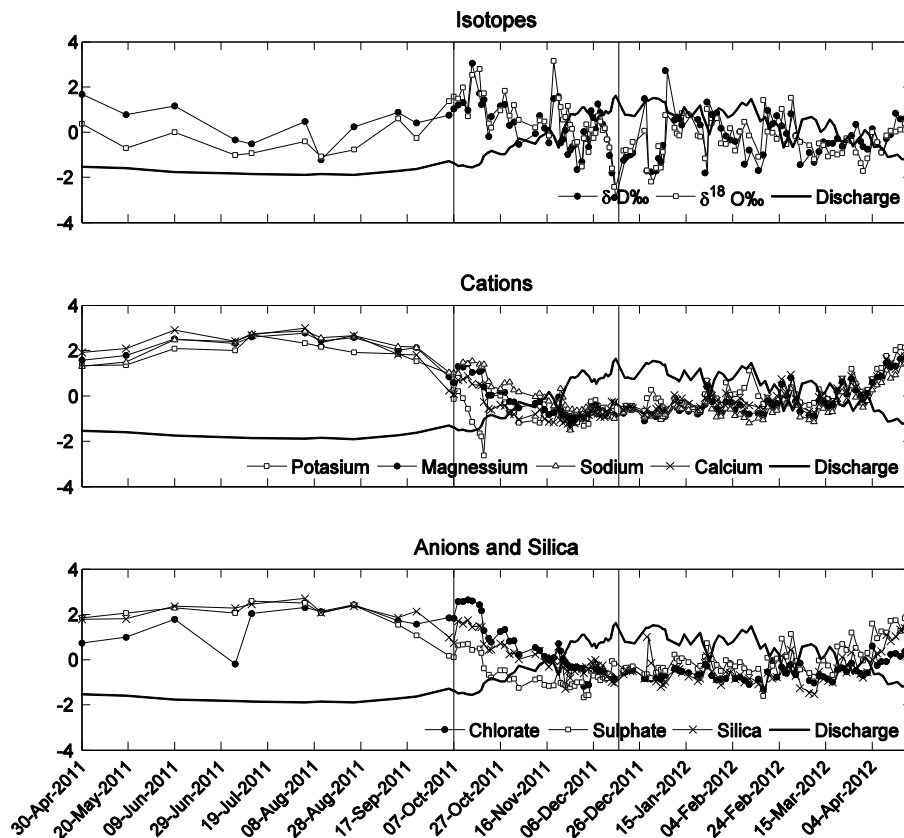
Figure 3. Centered and Scaled ions, isotopes and discharge data recorded by the sampler collector and Juncal at Juncal station.
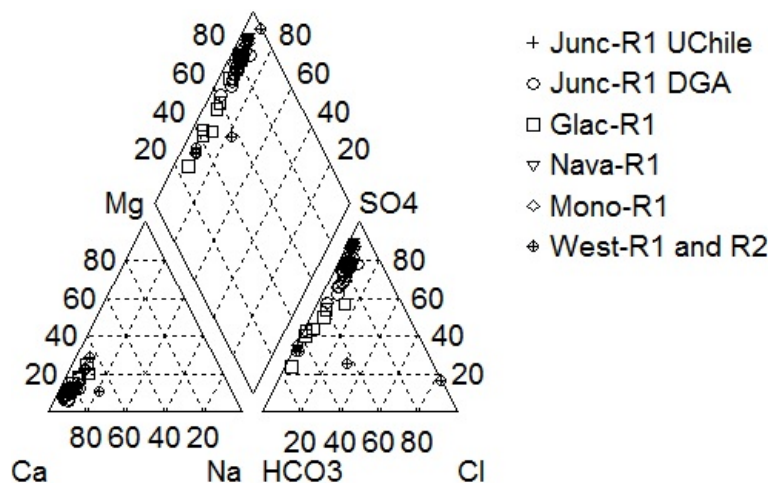
Figure 4. Piper diagram of Juncal Watershed samples.
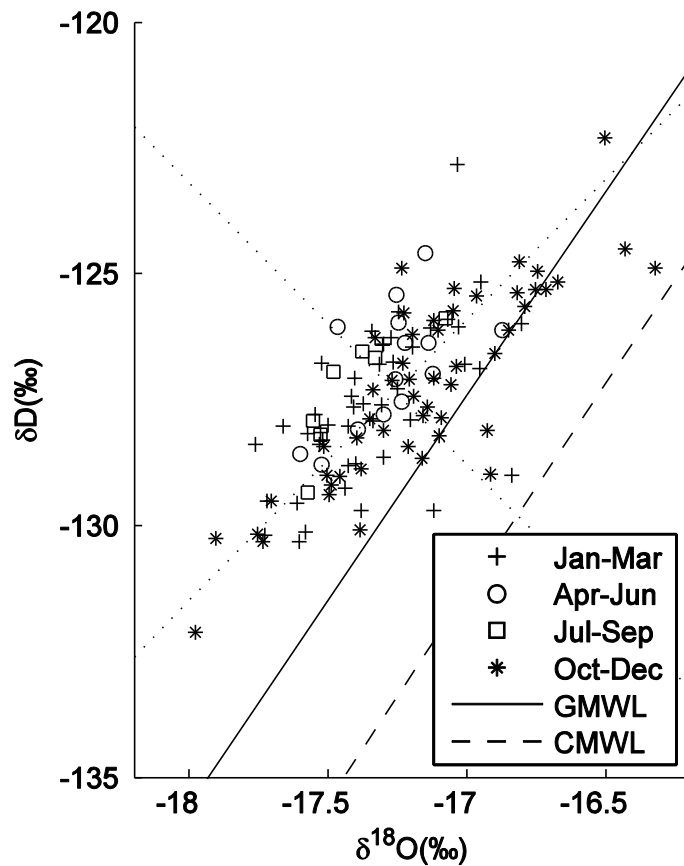
Figure 5. Deuterium and oxygen 18 graph. Dotted lines show first a second eigenvector obtained from PCA analysis. GMWL and CMWL refers to the Global and Chilean meteoric water line respectively.
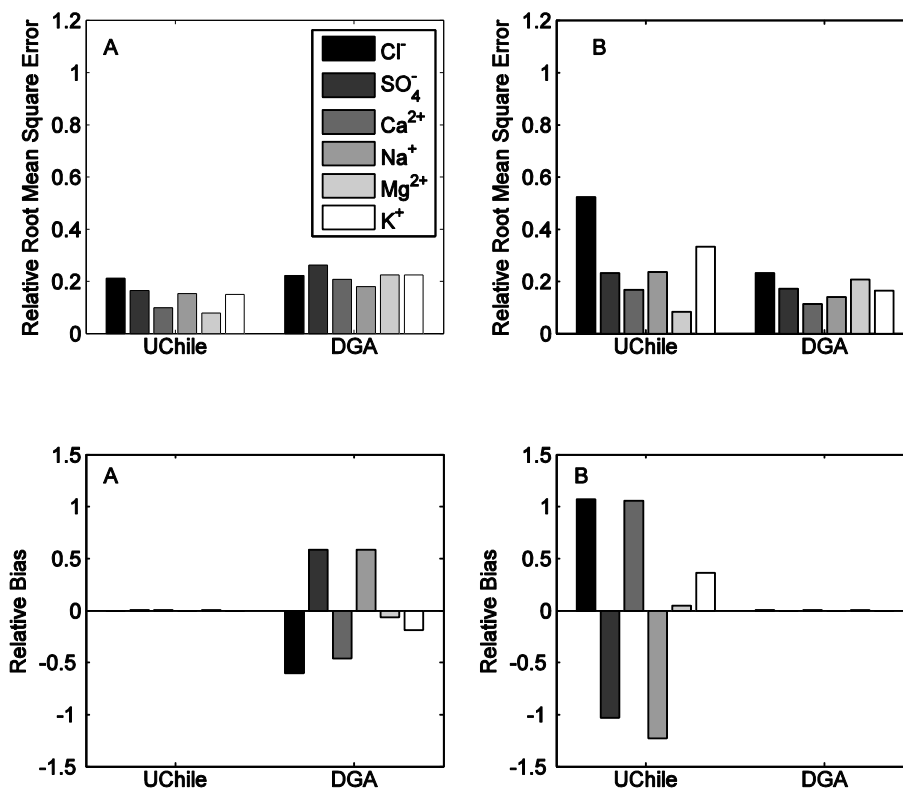
Figure 6. (A) R_{RRMSE} and B_{RB} in the U space constructed with UChile data. **(B)** R_{RRMSE} and B_{RB} of the U Space constructed with DGA data.
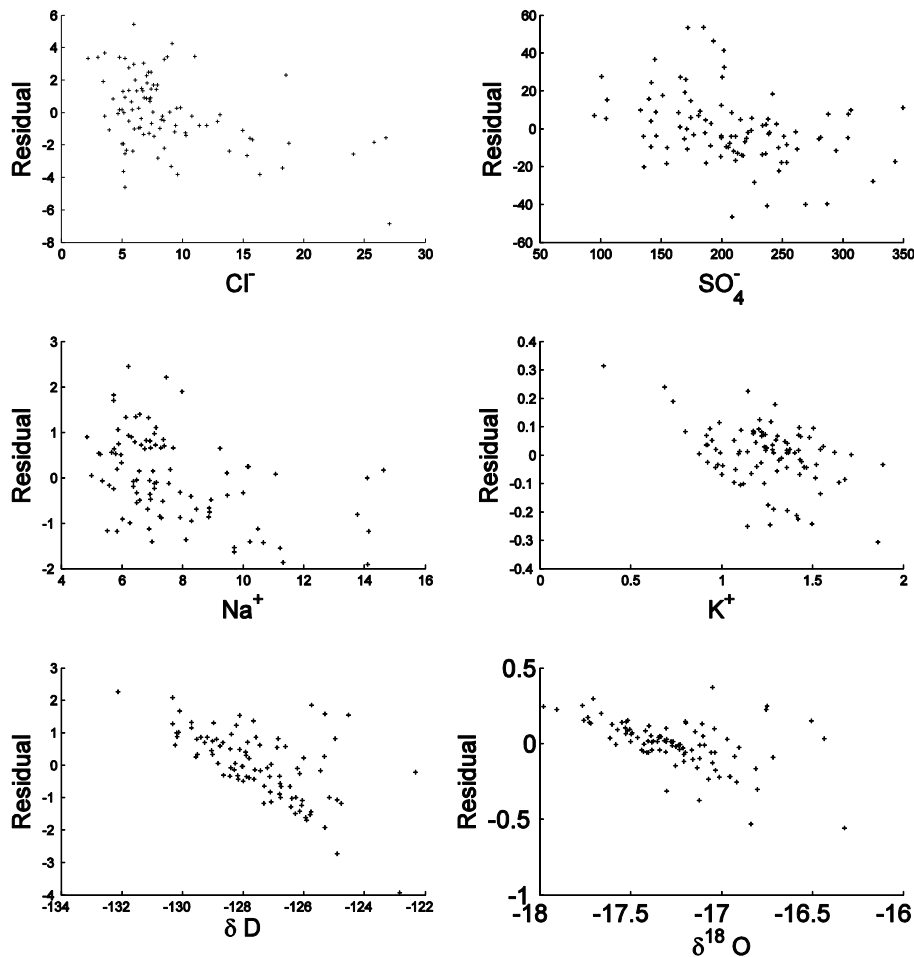
Figure 7. Residual on 2-D mixing space.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
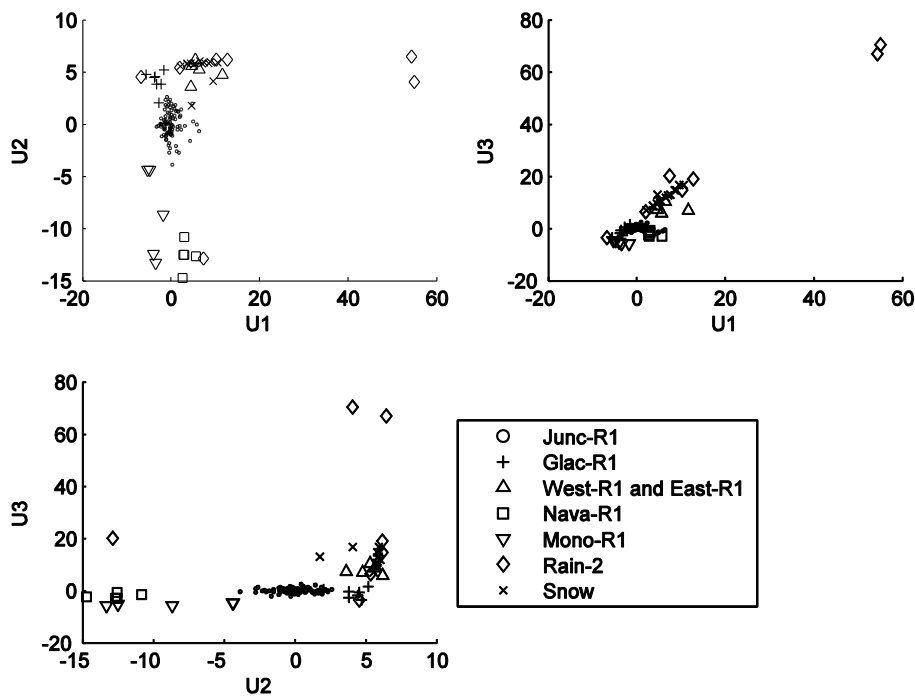
Figure 8. Planes of the 3-D *U* Space.
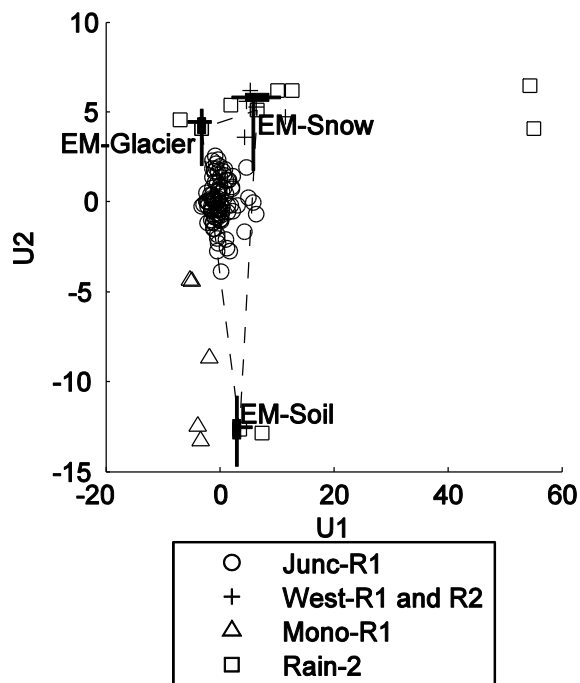
Figure 9. 2-D mixing U space. Bar represent interquartile of end-members selected.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Full Screen / Esc
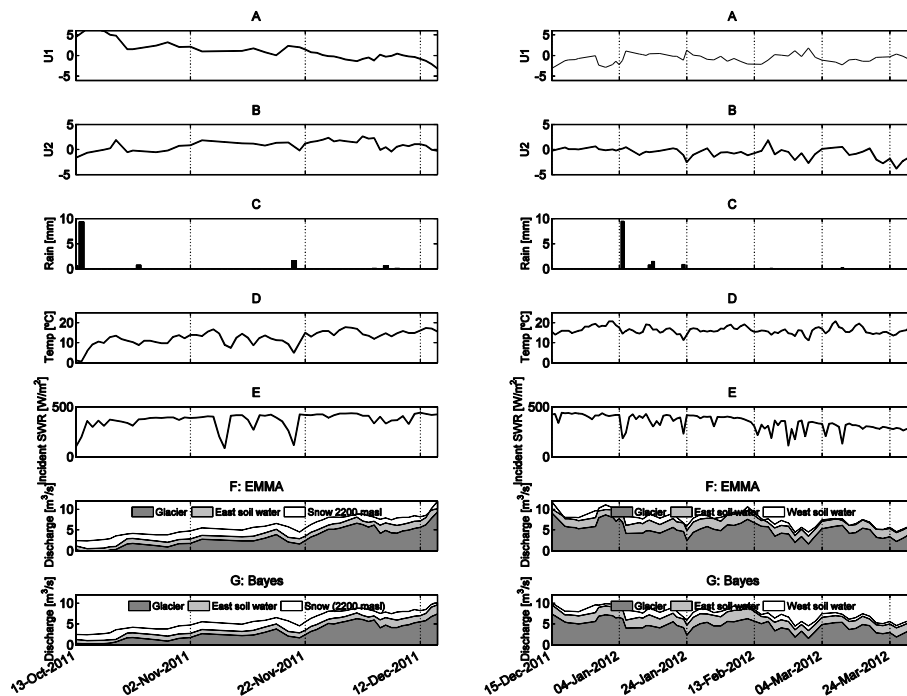
Figure 10. Hydrograph Separation on spring and summer. (**A** and **B**) shows Juncal data projected on eigenvector $U1$ and $U2$, respectively. (**C**, **D** and **E**) shows rain, temperature and incident solar short wave radiation on Hornitos. (**F** and **G**) depict hydrograph separation.
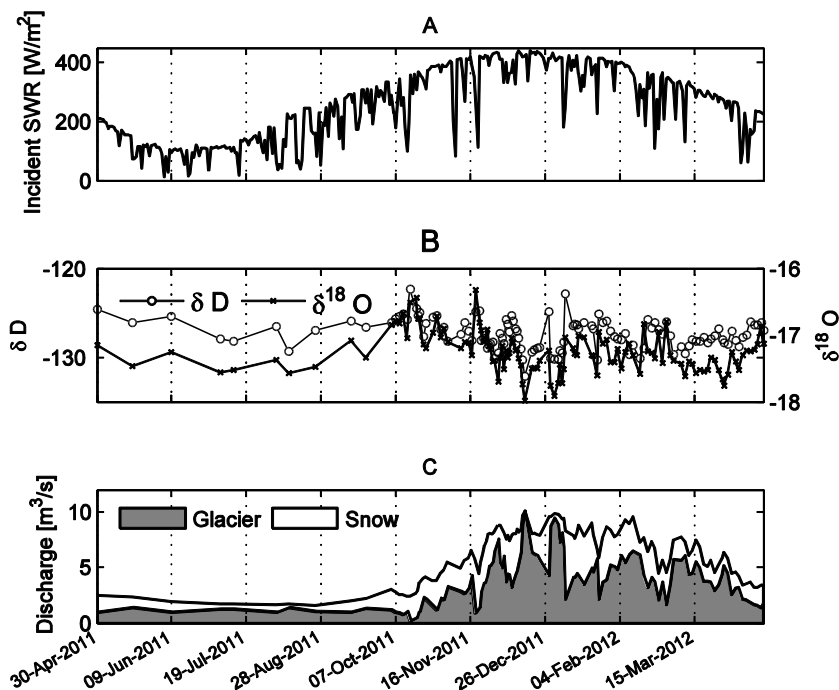
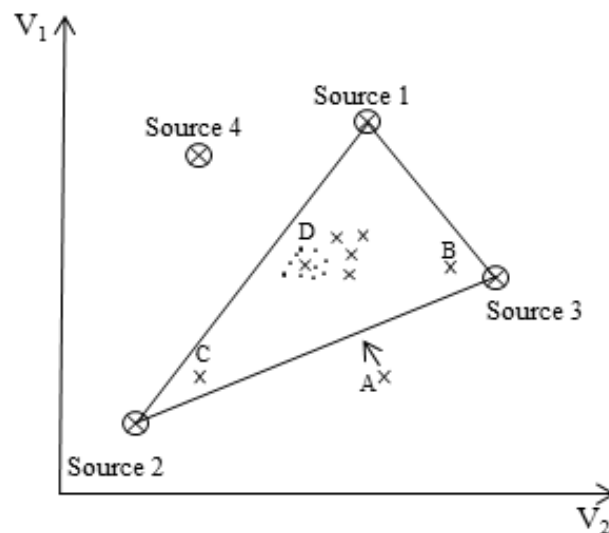**Figure 11.** Annual hydrograph separation using the Isotopic Model.

Figure 12. Conceptual plot in a hydrograph separation. Crossings represent Juncal outlet samples, points are a hypothetical sampling with MCMC and crosses with circle are sources.