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Stable water isotope variation in a Central Andean watershed dominated by glacierand snowmelt

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Received: 2 October 2012 – Accepted: 13 October 2012 – Published: 30 October 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Central Chile is an economically important region for which water supply is dependent on snow- and ice melt. Nevertheless, the fraction of water supplied by each of those two sources remains largely unknown. This study represents the first attempt to estimate the region's water balance using stable isotopes of water in streamflow and its sources; isotopic ratios of both H and O were monitored during one year in a high-altitude basin with a relatively high glacial cover (11.5%). We found that the steep altitude gradient of the studied catchment caused a corresponding gradient in snowpack isotopic composition and that this spatial variation had a profound effect on the temporal evolution of streamflow isotopic composition during snowmelt. Glacier- and snowmelt contributions to streamflow in the studied basin were calculated using a quantitative analysis of the isotopic composition of streamflow and its sources, resulting in a glacier melt contribution of 50-80% for the unusually dry melt year of 2011/12. This suggests that in (la Niña) years with little precipitation, glacier melt is an important water source for Central Chile. Predicted decreases in glacier melt due to global warming may therefore have a negative impact on water availability in the Central Andes as well as in comparable semi-arid regions of the world; this impact is non-commensurable with areal glacial cover or with the relative areal influence coverage of glacier versus seasonal snowpack. The pronounced seasonal pattern in streamflow isotope composition and its close relation to the evolution of snow cover and to discharge presents a potentially powerful tool for relating discharge evolution in mountainous, melt-dominated catchments with related factors such as contributions of sources to streamflow and snowmelt transit times.

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1.1 Hydrology in the extra-tropical Andes region – unknown inputs

Knowledge of the processes determining discharge in catchments dominated by glacier- and snowmelt becomes increasingly important as population and industrial activity increase in regions dependent on these water sources. Approximately one sixth of the global population derives much of its water from such melt-dominated watersheds (Barnett et al., 2005; Lemke et al., 2007). A region where water availability is especially important is the central part of Chile, which represents much of the country's growing economic production (Cai et al., 2003). This region is located between Mediterranean and semi-arid climates. Meteorological and hydrological conditions are similar to many semi-arid, mountainous regions of the world; extremely low precipitation during the summer months results in snow- and glacier melt from high altitudes being the main sources of streamflow (Cortés et al., 2011; Garreaud et al., 2009; Pellicciotti et al., 2005).

Globally, climate change has been projected to cause major changes in glacial-(Huss et al., 2008; Pellicciotti et al., 2010) and snow- (Graham, 2004; McCarthy et al., 2001) melt contributions to streamflow. So far, the processes governing accumulation and melt of snow and ice at high elevations in the extratropical Andes, including precipitation inputs, as well as spatial and temporal patterns of ice accumulation, transport and melt remain difficult to quantify and model. Although it is probably true that melt from the seasonal snowpack accounts for the bulk of runoff in the region (Masiokas et al., 2006; Pena and Nazarala, 1987), the actual contribution of glacier melt to the hydrologic regime remains a key component of the hydrologic cycle considering that (1) many high altitude catchments in the region have a relatively high percentage of glacial cover and (2) total annual precipitation shows high inter-annual variability, meaning that in dry years, snowmelt volumes could be reduced by as much as 50 % compared to an average year. Discharge evolution in extra-tropical, Andean catchments is further complicated by a seemingly long lag between melt and discharge of snowmelt waters.

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Typically, melt peaks during October or November in high altitude basins, whereas discharge peaks in December or January (Cortés et al., 2011). This might partly be due to a much later peak in the other main water source, glacier melt, which normally peaks in mid- to late summer (February–March for the Southern Hemisphere, Jost et al., 2012; Ragettli and Pellicciotti, 2012).

Isotopic studies of runoff and its sources have a large potential to shed light on these unknowns as stable isotopes of H_2O are natural tracers with potentially different compositions in snow- and glacier melt (Cable et al., 2011). The combined measurement of isotopic ratios in oxygen and hydrogen is especially powerful since the co-variation between the two in meteoric water sources can be affected by evaporation, sublimation, re-melting and exchange with atmospheric vapour (Ingraham, 1998).

Recent studies have pointed out the usefulness of isotopic data for assessing water transit time in catchments (reviewed by McGuire and McDonnell, 2006) but estimations of mean transit times in snowmelt-dominated systems are scarce. A recent study however (Lyon et al., 2010), used the duration of the snow-melt event, which caused a unique saw-tooth mark in the seasonal δ^{18} O pattern, for calculating the mean residence time of this snowmelt water within the catchment.

1.2 Isotopic variability in snow- and glacier melt

The stable isotope composition of river water is determined firstly by the conditions causing rain- and snowfall (mainly air temperature at the time of precipitation; Ingraham, 1998; Rozanski and Araguás, 1995) and secondly by evaporation and mixing during subsurface transport through catchments (Barnes and Turner, 1998).

During the last few decades, isotopic signatures of stream water have successfully been analysed to determine the source of stream water. Such studies have mostly focused on determining proportions of "old" or "pre-event" water and "new" or "event" water (e.g. Bottomley et al., 1984; Dincer et al., 1970). A large number of studies have also estimated snowmelt contribution to discharge (e.g. Laudon and Slaymaker, 1997; Laudon, 2004; Mast et al., 1995). However, few studies have fully recognized the large

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spatial and temporal variation in the isotopic signal of snowmelt. Taylor et al. (2001) presented the isotopic composition of meltwater in four different climates, and showed that snowmelt became isotopically heavier as the melt season progressed. This was due to preferential melt of lighter water molecules i.e. ¹⁶O and ¹H are initially released preferentially into the higher phase, a process that is analogue to fractionation during evaporation (Cooper et al., 1993; Rodhe, 1998). This process, from here on referred to as *isotopic elution*, causes enrichment (increase in δ^{18} O and δ^{2} H) through time in snowmelt and depletion in the remaining snowpack. Isotopic enrichment in snowmelt had a comparable range in all snowpacks studied by Taylor et al. (2001): approximately $4\% \delta^{18}$ O over a full melt season. Unnikrishna et al. (2002) found similar levels of enrichment during the snowmelt season. Cooper et al. (1993) showed that in hydrograph separation models, mixing of snowmelt with soil water is easily overestimated when the variation in isotopic fractionation of snowmelt is not accounted for. The latter study presented probably the most dramatic published change in stream isotopes caused by isotopic elution: streamflow showed an enrichment of 8% δ^{18} O throughout one week of snowmelt.

None of the above mentioned studies considered that the isotopic signal of streamflow is also affected by the spatial distribution of the snowpack and by snowmelt flowpaths (variation in transit time and flow route). A quasi-linear increase in snowmelt δ^{18} O and δ^{2} H through time is often assumed for streamflow, although snowmelt does seldom or never occur uniformly over catchments. In larger basins with much altitude variation, it should be assumed that for any given time, meltwater leaving the snowpack at different elevations is the result of different stages of snowmelt. For example, at a given time during snowmelt, an isotopically depleted signal from early-stage meltwater at high altitudes in streamflow might be compensated by isotopically enriched meltwater from low altitudes where snowmelt is in a later stage. Further, in large basins with a high elevation range, the average isotopic composition of the snowpack changes with altitude. The progressive isotopic depletion of precipitation is exacerbated by increased fractionation between liquid and vapour at low temperatures (Ingraham, 1998). The

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pre-melt snowpack will therefore have a more enriched average isotopic composition at lower altitudes.

Rozanski and Araguás (1995) presented stable water isotope data for precipitation in large parts of South America. They showed that the depletion of heavy isotopes with altitude followed two different patterns in the equatorial region and in the Andean region at 33° S (where our study catchment is located). In the tropics, the slope became steeper at high altitudes, whereas in the temperate Andean region the slope was steepest at around 1500 m (0.6 % /100 m) and substantially flatter at 2000–4000 m (0.2 % /100 m). As a comparison, Siegenthaler and Oeschger (1980) reported a 0.32 decrease in δ^{18} O per 100 m increase in elevation for the Swiss Alps.

Few studies have recognized the effect of such an altitude gradient on the isotopic variation in streamflow. As a working hypothesis for this research, we assumed that in catchments with large altitude ranges, spatial variation in the isotopic composition of the snowpack (causing streamflow to become *isotopically lighter through time* due to snowmelt originating from higher elevations) will affect the isotopic composition of stream water which is at least as large as the often observed isotopic elution phenomenon (causing streamflow to be *isotopically heavier through time* as snowmelt isotopic elution progresses).

Recently, some researchers have attempted to separate contributions of snow- and ice-melt to streamflow in mountainous basins using stable isotopes. Cable et al. (2011) included spatial and temporal isotopic variation of snow- and ice melt when identifying their respective contributions to streamflow. They determined the composition of discharge in terms of snowmelt, glacial melt and baseflow in a high elevation basin in Wisconsin, incorporating temporal and spatial variation of melting ice and snow into a hierarchical Bayesian model. In the studied basin, glacier melt contribution to snowmelt changed from 39 % in a high-flow year to 59 % in a year of low flow. Juszak et al. (2011 and unpublished data) combined stable water isotope and hydrochemical data to estimate contributions of glacier- and snowmelt, along with other runoff components in a study of the Haut Glacier d'Arolla glacier basin in Switzerland.

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Study objectives

The overarching goal of this study was to analyse the isotopic composition of streamflow in a high altitude basin and to estimate the contribution of the main sources comprising discharge in major periods during a hydrologic year. Further, we aimed to explore how stable water isotope data from stream water and its sources along discharge, temperature and other forcing time series can be used to explore hydrological processes occurring in semi-arid mountainous catchments, such as groundwater storage and precipitation events.

Study area, data and methodology

Study site description

The Juncal Basin (JB), comprises 256 km² of alpine, largely unvegetated (a sparse cover of predominantly low shrubs and meadows in the valley bottoms) terrain with an altitude range of 2200-5900 m a.s.l. (Fig. 1b). The catchment is located in the Aconcagua basin in the region of Valparaiso, Central Chile (Fig. 1a). The Juncal River, defined by the outlet at JR, is fed by three major tributaries, the glacial river to the south (JG), the Monos de Agua River to the southeast (JM) and the Navarro River (JN) to the east. The sub-catchments defined by these river nodes/sampling points are referred to as GB (Glacier Basin), MB (Monos de Agua Basin) and NB (Navarro Basin) respectively (Fig. 1). The southern and eastern parts of JB are located at higher altitudes, and contain most of the watersheds' 11.5 % glacial cover. Figure 2 shows hypsometric curves for JB and its sub-basins. It can be seen that MB and GB have much more of their area located at high altitudes compared to the total catchment (JB), whereas NB has an intermediate altitude distribution. MB has the highest area percentage located at altitudes between 3500 and 4500 m a.s.l., whereas JB has the highest percentage of very high (> 4500 m a.s.l.) altitudes. The Juncal Norte Glacier covers 10 km², and

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because of its dominant importance in terms of ice volume it was chosen for measurements of glacial melt. Figure 1 shows that the Juncal Norte glacier represents the largest continuous ice cover in the catchment.

The studied catchment experiences a Mediterranean, near- semi-arid climate with 5 an extreme concentration of precipitation during the winter months (Pellicciotti et al., 2005). Seasons are defined here as winter (June-August), spring (September-November), summer (December-February) and autumn (March-May). The warmest six months (October-March) are dominated by clear weather and high levels of incoming radiation. Therefore, precipitation above 2000 m a.s.l. falls mostly in the form of snow. At high altitudes, liquid precipitation occurs only during occasional convective storms (Garreaud et al., 2009). Low relative humidity throughout the year results in large differences between daily minima and maxima temperatures (typically ≈ 10 °C). At JR, average temperatures in summer are ~+15°C and in winter ~ +2°C. Precipitation shows a very strong interannual variability, influenced by the guasi-decadal ENSO sea surface temperature pattern (Pellicciotti et al., 2005; Rubio-Alvarez and McPhee, 2010; Waylen and Poveda, 1990). Considering very simplifed conditions, maximum snow accumulation is determined on the one hand by orographic lift causing increased precipitation on the windward slope of the Andes and on the other hand by steeper slopes and stronger winds near the crest causing less accumulation. This trade-off results in a precipitation maxima at around 3000 m a.s.l. on the windward slope of the Andes, below the crest, as is usually observed over high mountain range around the world. At higher altitudes and on leeside snow depth decreases sharply (Viale and Nuñez, 2011).

2.2 Streamflow monitoring and meteorological data

Standard hydrometeorological data was available from a network of stations operated by the Dirección General de Aguas (the Chilean water agency). These data include daily streamflow at JR, plus daily precipitation measured at the Riecillos meteorological station (32°55′22 S, 70°21′19 W, 1290 m a.s.l.) and daily air temperature plus

snow accumulation measured with a snow pillow at the Portillo station (32°50′43 S, 70°06′38 W, 3000 m a.s.l.). Additionally, meteorological data (air temperature, relative humidity, solar radiation) were obtained from the *Hornitos* weather station, located at JR and operated by the Mountain Hydrology Group at the Department of Civil Engineering, Universidad de Chile (Fig. 1). All data were collected and verified for a study period comprising an entire water year, from 30 April 2011 to 24 April 2012.

2.3 MODIS SCA data

Daily Snow Covered Area (SCA) data were obtained from satellite data supplied by the MODIS instrument aboard the TERRA satellite. The data is downloadable from the *NASA Reverb* website (NASA, n.d.) and supplies information of snow and cloud cover on a 500 m grid. Days with a high cloud-cover as well as sporadic snowfall events (< 3 days) were removed from the data set and linear interpolation was applied.

2.4 Isotopic sampling and analysis

An overview sampling protocol is provided in Table 1. Samples from the Juncal River were collected at JR, ca. 200 m. downstream from the DGA discharge gauge (Fig. 1). During the period of high discharge (5 October 2011 to 25 March 2012), samples were collected at either 24- or 48-h intervals, using a TELEDYNE ISCO 6712 automatic water sampler. A thin layer of mineral oil was added to all collection bottles in order to prevent evaporation from affecting the isotopic composition of the sampled water (Gazis and Feng, 2004). Manual stream samples were collected at least every three weeks, during the low flow season (April–September 2011) as well as complementary to automatic sampling during the high flow season (Table 1).

Manual samples were filtered in the field through a $0.45\,\mu m$ paper filter and stored in 15 ml plastic bottles without headspace. Upon returning to the University of Chile, samples were stored overnight at $+6\,^{\circ}C$. The following day, mineral oil and sediments were removed from automatic samples using $0.45\,\mu m$ paper filters. Samples were then

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poured into in 15 ml plastic vials and stored without headspace at +7°C until they were shipped to the Ehleringer lab in Utah, USA for isotopic analysis. We tested the effect of the added mineral oil layer by adding this fluid to samples of known isotopic composition and then immediately filtering and analysing those samples. Differences in both δ^{18} O and δ^{2} H before and after mineral oil addition were insignificant (p< 0.05). The same conclusion was made by Gazis and Feng (2004) and C. Gazis and X. Feng (personal communication, 2011).

A more limited number of samples of glacier melt, evenly distributed throughout the year, were collected at the basin headwaters (Table 1) because of limited accessibility and safety concerns (which prevented the installation of an automatic sampler). A total of nine samples of glacier melt were collected at the snout of the Juncal Norte Glacier (JG), while the outlets of the Monos de Aqua (JM) and Navarro (JN) tributaries were sampled on 6 and 7 occasions respectively.

Water seeping out of the ground at JS (2750 m a.s.l., Fig. 1) was sampled three times. This spring delivered a stable flow of water with a high electric conductivity (> 800 μS cm⁻¹ which was in the high range of measurements at JR) throughout the year and therefore probably represents relatively long-term aquifer storage.

Snow was sampled using a 2 m-length, 4.5 cm-diameter PVC tube in order to get a core representative of the total snowpack depth. The tube was gently pushed down through the snowpack until it reached the ground. The snow around the sampling tube was removed, and the sample was removed whilst covering the bottom of the tube with a gloved hand and then placed in triple plastic bags. When transported back to the field station, the samples were packed tightly together with cold water samples and were not allowed to melt. At the research station, the samples were melted overnight at 7°C, upon which filtration was carried out as with stream water samples.

In order to test our assumption regarding the altitudinal variation in the snowpack and melt isotopic composition, two snowmelt samples were collected at each 200 m elevation increment from 2200-3000 m a.s.l. The altitude gradient of snow samples were obtained on 10 August, following the road to the Argentinean border from the

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Portillo snow pillow ($3000\,\text{m\,a.s.l.}$) to JR ($2200\,\text{m\,a.s.l.}$). The range of elevations at which snow could be sampled was limited by the goal of obtaining all samples within the same day, and a more complete representation of the catchments' snowpack is the subject of future work. On 4 August 2011, 10 samples were collected along a micro-scale gradient (ca. $20\,\text{m}$ apart) at JR ($2200\,\text{m\,a.s.l.}$). Finally on September 13 and 21 direct samples of melting snow were collected at JR by placing a $3\times3\,\text{m}$ plastic sheet underneath the snowpack, from which snowmelt was funnelled into a collecting bottle. These samples represented the isotopic composition of snowmelt at a late stage of melt, because at the bottom of the catchment little snow (depth < $50\,\text{cm}$) remained on this date.

Rain samples were collected near the stream gauge (at 2200 m a.s.l., see Fig. 1) in a plastic bottle with a funnel and coarse paper filter attached. A thin layer of mineral oil was added before each collection, to prevent evaporation affecting the isotopic ratios of the collected rain water.

All water samples were analysed for oxygen and hydrogen stable isotopes using laser spectroscopy, at the isotope facility at Ehleringer lab, Department of Biology, University of Utah, USA. Lis et al. (2008) assessed the validity of this relatively new technique, with excellent results both in term of robustness and accuracy. The standard deviation of 10 analysis replicates was 1.1% for δ^2 H and 0.1% for δ^1 8O. The accuracy was 0.69% for δ^2 H and 0.11% for δ^1 8O. Analysis of 6 field replicates (JN samples collected immediately after each other) showed a standard deviation similar to that of the lab replicates, 1.22% for δ^2 H and 0.14% for δ^1 8O suggesting that the sampling routine introduced little error to our dataset.

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Meteorological characterization of the study period

For simplicity, in this paper we refer to years in which maximum snow water equivalent (SWE) at the Portillo snow pillow was ≤ 0.5 m and ≥ 1.0 m as "dry" and "wet" years respectively. Rainfall and discharge data show that the year of study was unusually dry. Based on precipitation records from the Riecillos station, the probability of exceedence of precipitation during the winter of 2011 was 85% (only 12 of 79 yr of record had less precipitation than 2011) and in 11 of 44 "melt years" (October-September) discharge from JB was smaller than in 2011/2012 (i.e. a probability of exceedence of 75% for streamflow).

Water balance estimates from historical runoff and meteorological data

In order to visualize the approximate contribution of snowmelt to runoff, compared to glacier melt, we plotted maximum winter SWE measured at the snow pillow at Portillo, against area-specific runoff from JB measured at JR (Fig. 3). For each point the xaxis represents the maximum SWE of a specific year and the y-axis shows runoff in the following "melt year" (October-September). Figure 3 shows that there is a good correlation between maximum SWE and JR runoff (p < 0.001), indicating (as expected) that annual snow input determines total runoff volume. However, the relationship has a large intercept on the X-axis; ca. 0.5 m of specific runoff, implying that other sources than snowmelt (mainly glacier melt) contribute significantly to runoff.

Assuming that glacier melt contributes approximately 0.5 m of specific runoff in dry years it can be estimated from Fig. 3 that glacier melt comprise nearly all runoff in those years. In years of higher precipitation, glacier melt may be reduced due to a longer period of snow cover. However, Huss et al. (2008) showed, for long-term data sets, that standard deviations of runoff from basins dominated by glacier melt were < 15 %. Assuming that total glacier melt volume does not change drastically between years, Fig. 3

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further suggests that in average years (i.e. at average spec. runoff; 0.84 m), glacier melt still is the dominant source, whereas in wet years, snowmelt contributes approximately half of runoff (rain contributions were excluded in this estimation). Water mass balance results produced by the distributed hydrological model TOPKAPI (Ragletti and Pellicciotti, 2012) for the same catchment, suggested as much as 80 % of snowmelt contribution to runoff for 2005/2006 which was a wet year. These contrasting estimates illustrate the uncertainties in the water balance of glacierised catchments in the region.

Figure 4 shows JR discharge for four years with different snow accumulation. The inserted table shows (spring and summer) runoff and precipitation data for the same years. It is evident from Fig. 4 that wet years have a different seasonal pattern, where discharge is high throughout the summer. The increase starts in early summer, assumingly at a point where soils are near-saturated with snowmelt waters, causing high volumes of stored meltwaters to leave the catchment. In the two dry years, discharge in summer stayed at a moderate level. Taking into account the conclusions from Fig. 3 above, we assume that in dry years, glacial melt and, possibly, the timing of sporadic rainfall events comprise the main controls of discharge variability throughout the summer season.

3.3 Stable isotope composition of river sources

Table 2 shows average isotopic composition for all sample types. It can be seen that snow samples at low and mid altitudes were highly enriched ($\delta^2 H = -121\%$) and depleted ($\delta^2 H = -134\%$) sources to JR ($\delta^2 H = -127\%$) respectively. Glacier melt ($\delta^2 H = -131\%$) was more depleted than streamflow but more enriched compared to mid-latitude snow.

Figures 5a–b show the isotopic composition of the snow cores collected along an altitude gradient plotted against altitude. Altitude significantly controls snowpack isotope composition. A relationship seems to be especially evident for elevations between 2600–3000 m, although if the regression line is drawn along those points, two of the low-altitude samples would be outliers. It is indeed possible that the two more depleted

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low-altitude samples should be removed from the data set because partial snowmelt occurs regularly on warm, sunny winter days at altitudes < 2500 m a.s.l. These lower values may therefore have been caused by meltwater entering the sample sites from surrounding hill slopes. Overall, the relation between altitude and isotope composition of precipitation was similar to that presented by Rozanski and Araguás (1995) who sampled precipitation and small rivers in Chile and Argentina. In our study, the average depletion with altitude was 0.44 %/100 m, or 0.56 %/100 m if the two more depleted low-altitude samples are treated as outliers and removed. Because there is still some uncertainty about the relationship between altitude and the isotope composition of snow we prefer to use two categories; low- (2200-2600 m a.s.l.) and mid-(2600-3000 m a.s.l.) altitude samples when discussing the influence of snowmelt on streamflow composition. The terms low- and mid-altitude refer to the catchment's altitude range; high altitudes (> 3000 m) were not sampled due to logistical limitations (see Sect. 2.4).

The lower diagram in Fig. 6 demonstrates the isotopic composition of collected snow and rain samples. The upper diagram magnifies the data which had values within the range of snow samples and includes the 9 glacier melt (JG) samples (white triangles). Rain (white circles) had an extremely wide range of isotopic compositions, from highly enriched precipitation that fell at high temperatures during summer and late spring, to isotopically depleted precipitation which fell at near-zero temperatures, therefore clustering with the snow samples. Altitudes at which snow samples (black stars) were collected are demonstrated in the figure. The samples for which no altitude is shown were collected near the stream gauge (at 2200 m a.s.l.). The two upper-right corner snow samples were direct samples of snowmelt collected in a late stage of melt. These were the two most enriched samples, demonstrating the often-observed effect that the later part of melt from a snowpack is isotopically heavier than early melt. This shows that the temporal isotopic change of snowmelt i.e. isotopic elution did occur. However, the large variation in 2200 m snow core samples, taken at various locations before the initiation of snowmelt, and the large difference between the two 2400 m samples (which

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were located less than 50 m from each other) shows that micro-scale spatial variation in snowpack composition might be as large as isotopic elution during snowmelt. In our data set therefore, the spatial gradient in terms of altitude was the dominant and most definable source of variation in the snowpack (see correlations between altitude and isotope composition in Fig. 5).

The isotopic composition of glacier melt (white triangles in the upper, magnified diagram of Fig. 6) show a relatively small degree of variation, considering that samples were collected at regular intervals throughout the year. All glacier samples had isotopic compositions similar to the two snow samples from $2800\,\mathrm{m\,a.s.l.}$, which is the elevation of the glacier tongue. The glaciers' accumulation zone is presently located $> 3000\,\mathrm{m\,a.s.l.}$ For a given altitude therefore, glacier melt appears to have a more enriched isotopic signal than snowmelt. The more depleted signal compared to snow at the same altitude suggested that measurements at JG was representative for glacier melt (at least from the Juncal Norte glacier) and little affected by snowmelt. Further, depleted isotopic values were not observed during periods of intense snow-melt at high altitudes (the lowest value, $\delta^2\mathrm{H} = -135\,\%$, was observed in autumn, on 30 April).

The isotopic composition of glacier samples, compared to the altitude gradient found in snow isotope composition has important implications for interpretation of streamflow sources. When air temperature rises in early spring, snowmelt is expected to start in the lower part of the catchment, resulting in meltwater with a relatively enriched isotopic signal, clearly distinguished from that of glacier melt (mean glacier $\delta^2 H = -131\,\%$), mean 2200–2600 m snow $\delta^2 H = -121\,\%$). In contrary, when snowmelt waters are most likely dominated by snow from higher altitudes, the snowmelt signal (mean 2600–3000 m snow $\delta^2 H = -133\,\%$) may be almost identical to, or even more depleted than, glacier melt.

All samples of sources to stream flow had a similar projection along the Chilean Meteoric Water Line (Fig. 6). Therefore, δ^{18} O/ δ^{2} H ratios do not seem to be a valuable indicator for separating sources (see ratios in Table 2). The most notable deviations

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were found in the late melt snow samples and summer (January) rain samples which were relatively lower in $\delta^2 H$ compared to $\delta^{18} O$.

3.4 Juncal River isotopic variation

3.4.1 Seasonal pattern

Figure 7 shows all JR samples, sorted by season, as well as all samples from the glacial (JG) and Monos de Agua (JM) tributaries. JN samples are not shown in the graph but had an average isotopic composition similar to that of JR. The average (positive or negative) difference for samples collected at JR and JN on the same day was only 1.24% for δ^2 H and 0.25% for δ^{18} O. MB has a high average altitude and a substantial glacial cover (15%), however much lower than that of GB (42%). It can be seen that most JM samples have a more depleted signal than JG, probably because of more snowmelt occurring at altitudes > 3500 m a.s.l. compared to glacier melt (see hypsometric curves in Fig. 2). JR samples all have values between the low- and mid-altitude snow samples. Most spring samples cluster towards the low altitude snow samples and most summer samples cluster towards the mid-altitude snow and glacier (JG) samples (cf. Fig. 6). JS samples had an isotopic composition similar to that of JG and mid-altitude snow, suggesting that soil water was affected by isotopic fractionation, due to evaporation and other factors, to a relatively small extent.

The evolution of streamflow $\delta^2 H$ in the Juncal River during the entire sampling period is displayed in Fig. 8 along with discharge, catchment SCA, precipitation and air temperature (the two latter recorded at the met station located at JR). Average $\delta^2 H$ of snow at low (2200–2600 m) and mid (2600–3000 m) altitudes are shown as lines and the two standard variations around the average glacier signal are shown as a hatched "belt" in Fig. 8 The temporal change in $\delta^{18} O$ is not presented as this data series showed a very similar pattern to that of $\delta^2 H$, but Table 2 below summarizes all isotope data. It should be noted that precipitation data is from the lowest part of the catchment (JR) where rainfall occurs less frequently than in the upper parts of the catchment.

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With the exception of episodic peaks in δ^2 H (more isotopically enriched water), the main patterns in JR δ^2 H variation were accompanied by changes in discharge. The isotope data in fact mirrors discharge data: δ^2H decreased when Q increased (October– December), then slowly increased (with the exception of episodic high values) towards a winter "baseline" as streamflow dropped towards winter baseflow (January-April). The decreasing trend in δ^2 H from -122% on 15 October to -132% on 15 December was accompanied by the regression of the snowpack as shown by the SCA data, which changes from 80 to 0 % within the same time period. The similar timing of (1) decrease in SCA, (2) increase in discharge from low winter levels to the first of two (> 10 m³ s¹) peaks and (3) distinct decrease in δ^2 H from the highest to the lowest observed value, suggests that the δ^2 H decrease was a result of streamflow being dominated first by melt of snow from lower altitudes and then progressively to a higher extent by higheraltitude snowmelt and/or glacier melt. Such an evolution of stream sources was expected but its signature in the isotope tracer was more pronounced than anticipated. The day-to-day variation in δ^2 H at JR was sometimes very large, with some peaks being especially prominent. These peaks were most probably results of episodic summer rain storms – rain during warm periods was highly enriched in δ^2 H (Fig. 6) and even small volumes of rainwater could therefore have caused these peaks. For example, the sharp increase in δ^2 H on 6 January (-123‰) coincided with a thunderstorm which caused intense rainfall on 5 January (9.4 mm in 3 h at JR, line 5 in Fig. 8).

The highest δ^2 H value (most isotopically enriched stream water), on 15 October (line 1), coincided with a local peak in SCA, just before rapid snowmelt started, as well as rainfall (snowfall above 2700 m a.s.l.), low temperatures and a flattening in the discharge curve, just after flow had started to increase. This peak in δ^2 H (-121 %) was partly due to rainfall (although rain fell at temperatures near zero: daily mean = 0.5 °C at JR) and partly a result of accumulated snowmelt from the first two weeks of melt in the lowest parts of the catchment. From this point, $\delta^2 H\%$ decreased along a line towards the dip value on 15 December (line 3), with exceptional peaks that were probably caused by warm rainfall, such as that occurred on 20 November (only 1.6 mm of

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rain according to JR data, but probably much more at high altitudes). Importantly, the dip in δ^2 H at line 3 is very close to the average glacier δ^2 H signal, does not reach the line indicating mid-altitude snow and is much more enriched than snow from 3000 m or higher. On 15 December, the snowline had been above 3700 m a.s.l. for more than 5 a month. Even if transit times were long, it is therefore very unlikely that snowmelt reaching the stream at this point in time came from altitudes lower than 3000 m. At this and all later sampling points therefore, streamflow was dominated by glacier melt. After the dip in δ^2 H (-132% on 15 December), the data set becomes highly varied, the lowest values staying within the reach of glacier melt while the majority of points form episodes of periodically increasing "waves" of isotopically much more enriched water. It appears most likely that during this summer period, glacial melt was the main source of runoff, the signal being frequently interrupted by warm rainfall which was probably not important in terms of water volume (rainy days did not affect Q), but had a pronounced effect on streamflow δ^2 H due to rainfall being extremely enriched in 2 H. If the peaks caused by rainfall events are cut out, it can be seen for the January-April δ^2 H data that as the hydrograph slowly recedes, the low range data points slowly increase towards winter values, which are relatively stable at around -126 %. This was interpreted as streamflow changing from being dominated by glacier melt to groundwater. During winter, discharge was continuously low (Fig. 8) and decreased slowly until the first days of spring snowmelt, pointing towards a winter hydrologic regime being controlled by slowly depleting groundwater, consisting of a mix of glacier melt and snow and rain from a variation of altitudes.

Epsiodic variability 3.4.2

Numbered lines in Fig. 8 point out episodes demonstrating how δ^2 H responded to a selection of interesting precipitation, discharge and SCA data points. At line 1, low altitude snow and rain initiated the melt period as described above. In the episodic δ^2 H peak at line 2, air temperature dropped and new snow covered the upper part of the catchment (see SCA data). The relatively high δ^2H was caused by snow from lower

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altitudes dominating streamflow composition as melt halted in the upper catchment, and possibly also by rainfall. The lowest observed δ^2 H value, at line 3, occurred just after the first (> 10 m³ s⁻¹) peak in discharge. This was most likely the last significant influence of mid- and high-altitude snowmelt, before glacier melt became the dominant source. The second discharge peak at line 4 is accompanied by a peak in temperature and is followed by a few δ^2 H points near the average glacier melt signal. Possibly, large parts of the glacier surface lost its snow cover during the first peak in Q line 3), causing highly enhanced glacier melt between line 3 and line 4. The δ^2 H peak at line 5 was most likely caused by the rainfall that occurred a few days earlier. From here on until line 7 (marking the end of the main summer period) the enrichment effect of summer rains gradually decreased. However, during a cold snap at line 6, glacier melt was possibly temporarily diminished, increasing the contribution of rain and/or groundwater causing an increase in δ^2 H. At line 7, discharge from the glacier dropped, causing aguifer and rain waters to push δ^2 H values upwards. At line 7, air temperature rose, causing δ^2 H to once again drop to a typical glacier signal. At the end of the measured period (no prec. and discharge data available), summer finally ended, causing $\delta^2 H$ to increase towards values near those observed in the winter period.

3.4.3 Diurnal variability

On 3 April 2012, the auto-sampler was set to collect a sample every 3h in order to monitor isotopic variation within a 24-h period. Figure 9 demonstrates that both isotopes showed a relatively high degree of variation within 24 h. This variability seemed to be defined by a sinus-shaped curve, peaking during the afternoon on 3 April and at 08:00 h in the morning on 4 April. The dip in both isotope tracers at 20:00 h on 3 April probably represents the largest concentration of glacier melt compared to aguifer storage water. This is because of the large diurnal difference in temperature and incoming radiation; on clear days air temperature peaks around 15:00 h, causing glacial melt to peak a few hours later; Q typically peaks between 18:00 h and 21:00 h at this time of

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the year. δ^{18} O data implies that depletion in this isotope started between 14:00 h and 17:00 h, whereas for δ^2 H, the switch to more depleted values occurred after 17:00 h.

Variation within 24 h probably caused some of the short-term (day-to-day) variation which can be seen in Fig. 9 although this effect was minimized by collecting all automatic stream samples at the same time each day (17:00 h).

3.5 Mass balance estimate using a quantitative analysis of water stable isotope data in streamflow and sources

The seasonal time-series of streamflow isotopic composition was relatively noisy (i.e. had a high short-term variability). However, distinct seasonal patterns in streamflow δ^2 H, compared to δ^2 H in sources, along with discharge, SCA and air temperature data, could be used to estimate the contribution of sources to streamflow within major periods.

3.5.1 5 April to 14 October 2011

Slowly decreasing streamflow throughout the winter period suggests that the dominant source to streamflow was groundwater. Groundwater contained a mix of glacier melt, snowmelt and a small contribution of rain. Our data does not allow for a percentage estimate of each source for this period, during which river flow represented 25% of annual streamflow.

3.5.2 15 October to 15 December 2011

During this period, in which runoff represented 24% of annual streamflow, the isotopic signal of JR changed from being close to the average of low-altitude snow, to being close to the signals of mid-altitude snow and to glacier melt; with the exception of rain events, δ^2 H dropped in a linear manner between 15 October and 15 December. For each of these dates, mass balance equations based on isotope data (Eqs. (1) and (2)

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$$\delta^{2}H_{\text{stream}}(\text{Oct 15}) = \text{CG} \times \delta^{2}H_{\text{glacier}} + (1 - \text{CG}) \times \delta^{2}H_{\text{(low alt.) snow}}$$
 (1)

$$\delta^{2}H_{\text{stream}}(\text{Dec 15}) = \text{CG} \times \delta^{2}H_{\text{glacier}} + (1 - \text{CG}) \times \delta^{2}H_{\text{(mid/high alt.) snow}}$$
 (2)

⁵ where; CG = glacier melt contribution to streamflow (1 = 100 % contribution).

Table 3 shows glacier melt contributions resulting from the above equations considering alternative definitions of low- and mid/high-altitude snow: Fig. 5a suggested an alternative correlation between altitude and snow δ^2H , where two points were treated as outliers and removed. Further, as the origin of snow on 15 December was unknown, 3 scenarios for the altitude origin of snow were considered (Table 3). Snow from 4000 m a.s.l. was calculated from the regression lines shown in Fig. 5a. Consideration of even higher altitudes did not change the result significantly.

Depending on the chosen isotopic composition of snow, Eqs. (2)–(3) resulted in glacier melt contributions of 8–45% and 62–98% for 15 October and 15 December respectively (see alternative scenarios in Table 3). The contribution of glacier melt therefore changed from 8–45% (low estimation) to 62–98% (high estimation) between these dates. As the different scenarios could be considered extreme low and high estimates respectively, 35–71% glacier melt contribution was considered a reasonable estimate for the total period.

3.5.3 15 December 2011 to 14 April 2012

After 15 December, $\delta^2 H$ at JR was continuously much higher than the signal of high altitude snow. The lowest values during this period are located near the average of JG data. Rain events interrupted this "base-line", causing peaks of highly enriched values. Although these enriched values represented most data points in the period, rainfall volumes were probably small as they did not cause any significant increases in Q. Our

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data does not allow for an exact calculation of glacier percentage during this period but indicates that the contribution of snowmelt was small; the increase in δ^2H after 15 December suggests an average glacier melt contribution during this period that was substantially higher than on that date (on which glacier melt already dominated streamflow). Therefore, glacier melt comprised at least 60 % of streamflow in this highflow period, which represented 51 % of annual discharge.

Validity and prominence of our results for water resources in semi-arid. mountanious catchments

Given our data, a quantitative analysis was the preferred method for defining seasonal and episodic stable isotope patterns in streamflow and comparing these to meteorological and SCA data. Using this approach, we were able to confirm that streamflow was dominated by glacier melt during the majority of the high-flow-period (> 5 m³ s⁻¹). The only time when snowmelt dominated was during spring and early summer.

With a high confidence we conclude that 50-80 % of streamflow was supplied by glacier melt in the studied year (see contributions during different periods in Table 4). This is a high percentage for a basin with a glacier cover of 11.5%, compared to published results from glacierised basins in other areas (Jost et al., 2012; Koboltschnig et al., 2008; Stahl and Moore, 2006; Verbunt et al., 2003; Zappa and Kan, 2007). It is also high compared to modelled results of the Juncal basin by Ragettli and Pellicciotti (2012), although data are difficult to compare as in that study, the model was applied during relatively wet years. However, compared to the conclusions drawn from historical meteorological and discharge data, our water balance estimate for a dry year seems reasonable (see Figs. 3 and 4 and subsequent discussion). Further, Gascoin et al. (2011) also found that the glacier contribution to streamflow was substantially larger than the percentage of glacier cover in the Huasco Valley (Chile, 29°).

The catchments of the two principal rivers in the region, Aconcagua and Maipo, presently have a glacial cover of 6% and 8% respectively (DGA, 2011). Given our results for a basin with 11.5% glacial cover, the contribution of glacier melt in dry

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years is most likely substantial for the total water supply in the region. If we assume that contribution of glacier melt to streamflow is approximately proportionate to glacial cover, our results for the Juncal catchment would suggest that total glacier melt contribution for the Aconcagua and Maipo basins in a dry year would be at least 30% of annual streamflow. Pena and Nazarala (1987) suggested glacier melt contributions of ca. 30 % for the Maipo basin during the most intense period of glacier melt (January-February) and 5-17 % during October-December for a year with total precipitation similar to 2011. Their study was based on a simple melt model using empirical temperature/radiation/streamflow relationships. Future research integrating various methods, basins, and years of study may explain the difference between our estimation of glacier melt contribution and the results from modelling studies such as those conducted by Pena and Nazarala (1987) and Ragettli and Pellicciotti (2012).

Our study confirms that in the year of study, glacier melt was an extremely important water source, comprising more than a third of streamflow in a region where glacier cover is < 10 %. Glacial retreat has been observed in the Central Andes (Rabatel et al., 2011; Rivera et al., 2002): the Juncal Norte glacier exemplifies this well with a retreat of 0.35 km² (3.5%) in the period 1999 to 2006 and much more during the last century (Bown et al., 2008). Considering that long-term losses in glacier melt volumes have been predicted (Huss et al., 2008; Pellicciotti et al., 2009), water availability in the studied region and other semi-arid mountainous areas of the world may decrease substantially in future dry years.

Conclusions and directions for further research

In this study of isotope variation in a high-altitude melt-dominated Andean catchment we draw conclusions that complement earlier studies on the subject and add novel information about the hydrology of this environment:

Firstly, although evidence of isotopic elution could be seen in snow data (late-stage snowpack meltwater was isotopically more enriched than pre-melt

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snowpack), the largest source of isotopic variation in snow was undoubtedly the catchment's steep altitude gradient, causing a distinct pattern in streamflow isotopic composition. It proved difficult to interpret in great detail how this "snow altitude effect" controlled the isotopic composition of streamflow, since mid-altitude (2600-3000 m) snow had isotopic values similar to those of glacier melt. Further research is needed in order to refine this characterization.

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Secondly, in the studied catchment and year, glacier melt rather than snowmelt was the dominant source to streamflow at all times of high (> 50 % of peak) discharge. For the melt season, snowmelt was unequivocally dominant only during spring (mid-October to mid-November). An approximate mass balance calculation estimates that 50-80% of the Juncal River streamflow consisting of glacier melt during the studied period (one year). Our estimate is consistent with a revision of historical streamflow and meteorological data and implies that in dry years (which are relatively frequent) glacier melt is a highly significant water source in the Aconcagua basin, and very likely in neighbouring watersheds with similar characteristics as well. Long-term decreases in glacier melt volumes due to global warming could therefore result in a dramatic decline in water availability for Central Chile, especially in years of low precipitation.

A qualitative analysis of streamflow isotopic variability combined with detailed analysis of sources such as performed here is a valuable source of additional information, the results of which may be compared with and assimilated into hydrological models of varying complexity in order to shed light on the interplay of mechanisms governing flow variability in semi-arid, melt-dominated rivers. Such future studies have the potential to increase our knowledge on the importance of glacier melt to streamflow and further, to predict consequences of glacier ice retention for water availability in semi-arid regions as well as to inform adaptation strategies to climate change for communities existing in such environments.

A desirable follow up of this research would include the application of stable water isotopes for detailed hydrograph separation on a daily or weekly scale. In order for this goal to be achieved, our results suggest that the following challenges must be addressed:

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- We did not observe a difference in the average $\delta^2 H/\delta^{18} O$ ratio of major sources. Other tracers such as hydrochemical data could improve the performance of separation models such as EMMA or Bayesian Mixing models. Upcoming research will refer to this issue.
- The isotopic composition of snowmelt changes with altitude and therefore with time during snowmelt. This issue may be partly overcome in mixing models by letting snowmelt input change over time. However, even if the location of the snowline at each point in time is known, the uncertainty regarding snowmelt transittimes is a difficult problem to overcome.
- Glacier melt had an isotopic signal between that of low- and high altitude snow, meaning that a mixing-model will have substantial problems separating these sources. A more detailed analysis would require data of different types and sources, assimilated into more complex mixing or hydrochemical models.
- Just like snow, rain will also have a large difference in the isotopic signal between altitudes. Its isotopic signal will be distributed along a line from more depleted values in cold, high-altitude rain to more enriched values in warm, low-altitude summer rain. A distributed experimental network of rain gauges could alleviate the problem of characterizing this spatial variability. On-going research will address this topic.

The distinct pattern in the stable water isotope tracer data, observed in the Juncal River during spring to early summer (caused by snowmelt from increasingly high altitudes and higher contributions of glacier melt) allows for interpretation of snowmelt

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transit time and connections between catchment hypsometry and discharge evolution. Such data collected in comparable rivers and in years with different snow accumulation, combined with SCA and meteorological data, could be an excellent tool for exploring how runoff mechanisms and sources change through the snowmelt season and how they are controlled by catchment geomorphology and snowmelt input from different altitudes. For example, in catchments with similar hypsometry, storage times could be compared using the degree of dampening in the snowmelt isotope pattern (cf. Asano and Uchida, 2012). In catchments without a significant glacial cover, elimination of the glacial signal would ease the analysis of transit time and snowmelt evolution.

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Table 1. Overview of all samples collected in the study.

	AUT	UMN	'	WINTER	3		SPRING	à	5	SUMME	R	AUT	UMN
Sample Type	Apr 2011	May 2011	Jun 2011	Jul 2011	Aug 2011	Sep 2011	Oct 2011	Nov 2011	Dec 2011	Jan 2012	Feb 2012	Mar 2012	Apr 2012
JG	1	1	-	_	_	-	1	1	-	2	_	1	2
JM	1	1	<u> </u>	_	_	-	1	1	<u> </u>	1	_	-	1
JN	1	_					1	1	<u> </u>	1		1	2
JS	_	_	<u> </u>	_	_	-	_	_	<u> </u>	1	_	1	1
Rain	_	_	-	_	_	2	2	2	-	2	_	1	1
Snow cores (altitude gradient)	_	_	_	_	10	_	_	_	_	_	_	_	-
Snow cores (2200 m a.s.l.)	_	_	_	_	10	_	_	_	_	_	_	_	-
Snowmelt	_	_	_	_	_	2	_	_	_	_	_	_	_
JR manual	1	1	1	2	3	2	3	2	1	2	_	-	2
JR (auto)	(continuously at 24 – or 48 h intervals)												

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Table 2. Average δ^2 H and δ^{18} O in all sample types with standard deviations.

	JR	JG	Rain	Snow 10/8 average for 2200–2600 m	Snow 10/8 average for 2600–3000 m	Snow 4/8 (2200 m)	JS	JM	JN
n-samples	127	9	10	6	6	10	2	6	7
Average δ^2 H (‰)	-127	-131	-74	-121	-134	-110	-134	-136	-127
St. Dev. δ^2 H (‰)	1.6	2.6	52	7.4	12	4.4	0	1.8	1.25
Average δ^{18} O (‰)	-17.3	-17.9	-10.9	-16.2	-17.9	-15.2	-18.1	-18.3	-17.1
St. Dev. δ^{18} O (‰)	0.29	0.38	6.6	0.87	1.45	0.66	0.12	0.35	0.23
Ratio δ^{18} O δ^{2} H	0.136	0.137	0.147	0.135	0.134	0.138	0.135	0.135	0.135

Table 3. Contribution of glacier melt to streamflow on 15 October and 15 December 2011 according to different interpretations of snow isotope data.

Altitude/snow δ^2 H relationship	Altitude used for snow signal on 15 Dec		elt contribution amflow (%)
		15 Oct	15 Dec
	2600-3000 m a.s.l. (mean)	8	71
with outliers	3000 m a.s.l. (regression line)	8	88
	4000 m a.s.l. (regression line)	8	97
	2600-3000 m a.s.l. (mean)	45	62
without outliers	3000 m a.s.l. (regression line)	45	90
	4000 m a.s.l. (regression line)	45	98

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Table 4. Contribution of glacier melt to streamflow in three different periods and during one year.

Period	Glacier melt contribution to streamflow (%)	% of annual flow
14 Apr-15 Oct 2011	?	25
16 Oct-15 Dec 2011	35–71	24
16 Dec 2011-14 Apr 2012	> 60	51
TOTAL	50–80	100

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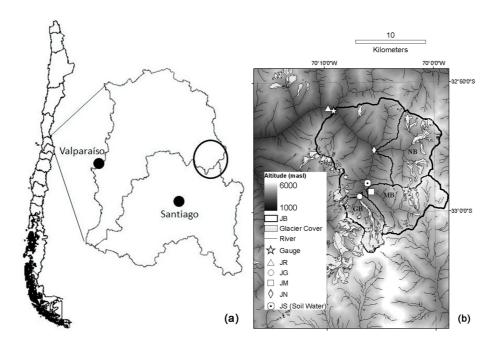


Fig. 1. (a-b) Study area with locations of stream gauge and water samples.



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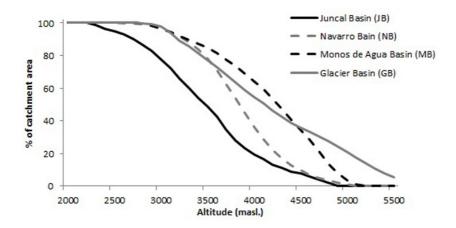


Fig. 2. Hypsometric curves for JB and the three main sub-catchments (NB, MB and GB).

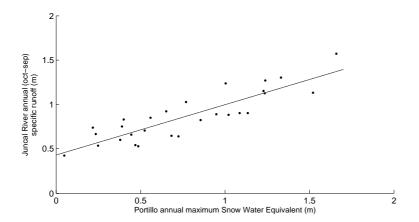


Fig. 3. JR total annual specific runoff (October year x to September year x + 1) plotted against maximum winter Snow Water Equivalent at the Portillo meteorological station in each corresponding year (x). Data for 28 yr between 1970 and 2009 is presented.

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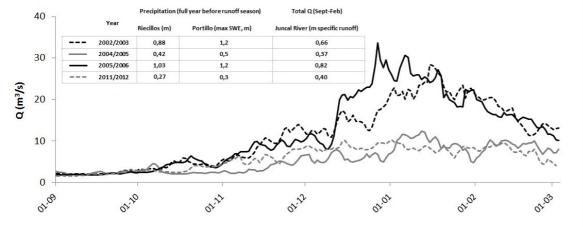


Fig. 4. Juncal discharge in two wet and two dry years. The inserted table shows precipitation data and cumulative discharge for the same example years.

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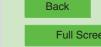
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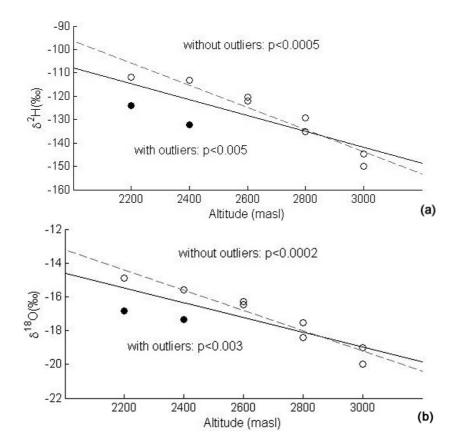


Fig. 5. (a–b) Relationship between δ^{18} O (a) and δ^{2} H (b) and altitude of snow-cores collected along an elevation gradient (2200-3000 m a.s.l.), along the road to the Chile-Argentina border, just northeast of the studied catchment. In an alternative correlation (dashed line), black points were treated as outliers and removed.

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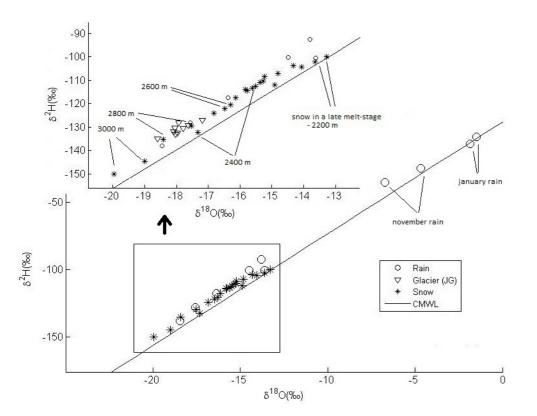


Fig. 6. Isotopic composition in samples of glacier melt, rain and snow in the study area. CMWL is a line representing the δ^{18} O/ δ^{2} H relationship defined as the Chilean Meteoric Water Line.

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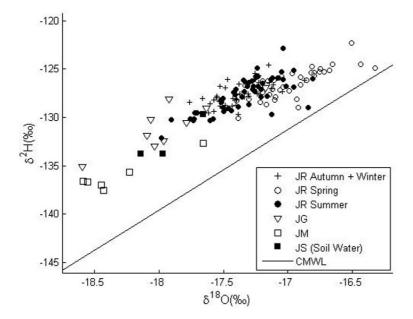


Fig. 7. Isotopic composition of water samples from the Juncal River (JR) and from the glacier (JG) and Monos de Agua (JM) tributaries. JR samples are grouped by season; Autumn = March-May, Winter = June-August, Spring = September-November, Summer = December-February.

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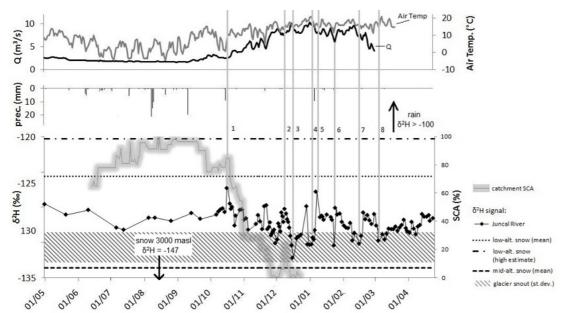


Fig. 8. Temporal variation in $\delta^2 H$ in the Juncal River during the study period (May 2012– April 2012), with average values for low- (2200-2600) and mid- (2600-300) altitude snow and standard deviation of glacier melt. The figure also shows catchment SCA and discharge, precipitation and air temperature at JR.

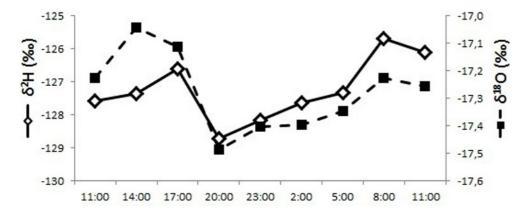


Fig. 9. Variation in δ^2 H and δ^{18} O during 24 h in the Juncal River. Samples were taken every three hours between 11:00 h (3 April) and 11:00 h (4 April) 2012.

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