Snow Stable Isotope Composition Variability Related to the Upper Mendoza River Basin Hypsometry

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Abstract: *The water supply of the northern oasis of the Mendoza province, in the central western of Argentina, depends mainly on the melting of precipitated and accumulated snow during the winter, which supplies water for domestic, industrial and energy consumption to 64% of the provincial population (more than 1.2 million inhabitants). The solid precipitation stable isotopes composition in mountain regions is affected by isotopic fractionation processes generated by continentally effects, temperature, evaporation during precipitation and isotopic elution phenomena during melting, among others, complicating efforts to quantify sources using stable isotopes as natural tracers. The aim of this work was to evaluate the stable isotopes composition of snowfall in an altitude gradient in the Cordillera Principal, Upper Mendoza River basin. We did not find an altitude effect on stable isotope composition of snow, widely reported in previous studies. Variability was related to the origin of precipitation events. These results validate the use of stable isotopes as tracers of different water sources as glaciers, permafrost, groundwater or snow in Cordillera Principal, to quantify contributions from different sources to river flow.*

Keywords: *stable isotopes, snow, Cordillera Principal, Mendoza River*

1. INTRODUCTION

The predicted near surface warming under the influence of increasing levels of greenhouse gases in the atmosphere will be particularly greater in mountain regions (Bradley et al., 2004), with important consequences for the hydrological cycle, particularly in regions where water supply is dominated by the melting of snow and ice, as is the case of the irrigated oases in the Mendoza province (Masiokas et al., 2013). The high glacial melt rates documented in recent decades at global (WRCP, 2009; wgms, 2013) and regional levels (Leiva 1999; Bown et al., 2008) corroborates this increase in the global average temperature, since the industrial revolution. With deeper expected increases in temperatures and droughts for the region (Bradley et al., 2004; Corripio et al., 2007; Gonzalez-Reyes et al., 2017), it is important to monitor the hydrological evolution, including changes in the relative importance of different water sources to river flows. Water stable isotopes, offers an important tool to trace the different water inputs to a river in a basin.

Isotope fractionation is responsible for the changes in the water stable isotope composition when change from one phase to another (Hoefs, 2015). In the hydrologic cycle, water vapor has as its main source oceanic water, from which much of it evaporates, moving towards higher latitudes and altitudes where it cools and condenses precipitating in the oceans. Another part of the vapor advances towards the continent precipitating and forming superficial and subterranean waters. During the condensation process, which results in the precipitations, the fraction of vapor remaining in the air is progressively impoverished at ^{18}O and ^{2}H, whereby the values of $\delta^{18}O$ and $\delta^{2}H$ of the water vapor become progressively more depleted as precipitation occurs. This is because, as atmospheric humidity cools,

the heavy molecules condense more easily and the residual vapor contains less and less heavy isotopes. In this way, the meteoric waters leave a characteristic mark, fundamental for the studies of waters (Clark and Fritz, 1997).

In mountains, particularly, isotope fractionation is associated to altitudinal gradients, in a process similar to a Rayleigh fractionation, caused by the preferential precipitation of heavy isotopes in low altitudes, when moist air masses are forced to ascend by these geological barriers. The consequence is a gradient of decreasing natural abundance of heavy isotopes with increasing altitude, observed in many mountain areas of the world (Mariani et al., 2014; Windhorst et al., 2013; Poage and Chamberlain, 2001; Schotterer et al., 1997; Niewodniczanki et al., 1981; Siegenthaler and Oeschger, 1980). Generally, the $\delta^{18}O$ impoverishment, varies between -0.15 to -0.5 ‰ per 100 m increase in altitude, with a corresponding -1 to -4 ‰ δ^2H value decrease (Clark and Fritz, 1997). This altitudinal effect is related to the temperature, since condensation is produced with the decrease of the temperature, while altitude increases. Because of the decrease in pressure with altitude (-1.2% per 100 m; Mook, 2002), a lowering of the temperature is required to precipitate than in the case of isobaric condensation, to reach saturated water vapor pressure. This force the precipitation occurrence in a cooler environment and more isotopically depleted signatures in snow are expected to be linked to hypsometry increase.

Stable isotopes and ions are useful natural tracers of snow, glacial, groundwater and rains in the study region (Crespo et al., 2017), showing a clear differentiation among these different water sources. However, the expected variability of the isotopic composition of snow, given by fractionation during the evolution of atmospheric moisture along its path from oceans to precipitation sites, presents a challenge to the application of these tracers in snow tracing for the leeward side of the Andes. Moisture is derived from the Pacific, which ascends the Andes in the windward side of the mountains, in the Chilean Andes side, where a Rayleigh type fractionation occurs (Rozanski and Araguás, 1995; Ohlanders et al., 2013). This dynamic change when precipitation reaches the leeward side, in the Argentinean side of the Andes, where other processes may affect stable isotope composition of snow, which are expected to be unrelated to altitude (Crespo et al., 2017).

This work seeks to evaluate the relationship between altitude and stable isotope composition of snow in the leeward side of the Andes, to use stable isotopes as tracers of snow contributions to the tributaries of the Cordillera Principal. In order to test this relationship, we sampled snow that had precipitated in different altitudinal levels, and determined the stable isotope composition of the samples.

With this characterization, we expected to reach a more complete knowledge of each water component in the mountainous hydrological cycle, complementing the study of basin contributions with different types of glaciers, snow and groundwater developed in Crespo et al. (2017). This knowledge will contribute information to evaluate water scarcity mitigation policies in the near future.

2. METHODOLOGY

2.1. Study Area

The main criterion to select the study site was to analyze a basin that was important for the population water supply. The Mendoza River supplies more than one million people with only 49 m^3 / s of average monthly flow (Masiokas et al., 2013). Vitiviniculture represents the second economic activity of the province after the hydrocarbon industry (Corripio et al., 2007) and relies on irrigation. Between 1986 and 2003, 62 % of the energy for domestic use was generated by the runoff of the mountain rivers (Masiokas et al., 2006). These data indicates that the socio-economic development and the subsistence of the central-western region of Argentina are strongly linked to the melting waters of the Andes.

The Mendoza River flow derives mainly from the winter snowmelt, which is strongly influenced by high interannual variability (Minetti et al., 1986; Bruniard, 1994; Compagnucci and Vargas, 1998; Masiokas et al., 2006). In these latitudes the maximum amount of precipitation is observed in the windward, in the Chilean side of the Cordillera Principal mountain range. Rainfall increases from 300 mm per year on the Chilean coast to over 700 mm above 2885 masl in El Portillo, Chile, a few kilometers before the international limit. From the Argentine-Chilean boundary to the east, precipitation amounts decline rapidly, generating a large gradient while they cross the mountains, with

less than 300 mm in the inmediate leeward slope, to less than 50 mm in Uspallata, at 1891 m asl (Viale and Nuñez, 2011).
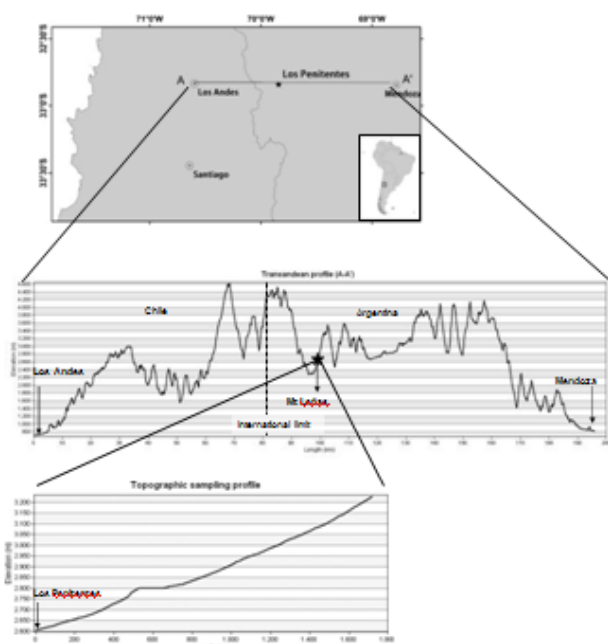

Figure1. *Site map and elevation profile of the sampling altitudinal transect developed at the Mt. Leñas*

2.2. Snow Sampling in Cordillera Principal

Isotopic composition modifications occur during continental transport, precipitation, accumulation period and / or water delivery, and thus the snow isotopic composition studied (eg, Ohlanders et al., 2013; Dietermann and Weiler, 2013; Rodriguez et al., 2014; Crespo et al., 2017) are not known with precision, especially concerning the stable isotopes composition changes related to altitudinal effect. Considering the precipitation gradient along the West-East direction explained before, the sampling design includes snow samples taken in an altitudinal transect (Fig. 1) located on Mt. Leñas (32 ° 49 '30.24 "S, 69 ° 50' 03.06"W), in the Cordillera Principal geological province, after two storm events during the winter 2016. This sampling design is coincident with the accumulation period of the winter snowfall.

The samples were collected in 15 mL falcon tubes, sampling the snow accumulated in two snowstorms, on June 25th and July 2nd, 2016. To avoid fractionation, samples were taken early in the morning, before temperatures were above 0° Celsius and sealed with a cohesive thermoplastic (PARAFILM). They were taken along an 1800 m transect, at 100 m altitudinal intervals, in seven sites located from 3214 to 2614 m asl. To prevent fractionation during sublimation and snow melt as much as possible, a minimum of time should elapse between each sampling at each altitudinal level sampled. Therefore, samples were taken by skiing and the temperature of the snow was recorded with an infrared thermometer, where the temperature of the snow sampled was never warmer than -1° C.

2.3. Chemical Analysis

Isotopic analyzes were determined by laser spectrometry using the T-LWIA-45-EP (Triple Laser Water Isotope Analizer) of Los Gatos Research at the Stable Isotope Laboratory, Andrés Bello University. The measurements presents an error lower than 0.80 for δ^2H ‰ and 0.10 for $\delta^{18}O$ ‰, according to the Vienna Standard Mean Ocean Water (VSMOW) (Table S1, Supplementary data).

2.4. Statistical Analysis of the Altitudinal Influence on the Content of Water Stable Isotopes

The effect of altitude on the isotopic compositions (δ^2H, $\delta^{18}O$ and deuterium excess) of snow was analyzed with a generalized linear analysis (Burnham and Anderson, 2002), in R statistical environment (R Core Team, 2013).

2.5. Modeling Retro-Trajectories of Air Masses

In order to determine the origin of the air masses that cause precipitation in the Mt. Leñas, a data analysis is carried out to obtain the trajectory of the precipitations analyzed: June 25th and July 2nd, 2016.

The modeling is based on a retro-trajectory analysis of the air masses that precipitate in the study area, using the free-use software HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory, (Draxler and Hess, 1998), a resource shared by the Air Resources Laboratory (ARL) of NOAA (National Oceanic and Atmospheric Administration).

A daily analysis of the data was carried out using the Global Forecast System (GFS) database with a quarter degree resolution, obtaining a 72 hours retro-trajectory, in a constant pressure test (approximately 520 mbar, equivalent to 1500 masl), running the model at 12 pm (local time) each day.

3. RESULTS

3.1. Water Stable Isotopes Composition

Firstly, a difference in the isotopic composition in each storm event was observed, with lower δ^2H and $\delta^{18}O$ values in the later one (B). The snow isotopic composition represents a Local Meteoric Water Line (LMWL) following the equation: $\delta^2H = 7.52 \, \delta^{18}O + 2.66$, with an $R^2 = 0.99$. This trend line is slight different, especially in the intercept, than the Global Meteoric Water Line (GMWL) defined by Craig (1961), which follows the equation: $\delta^2H = 8 \, \delta^{18}O + 10$ (Fig. 2).
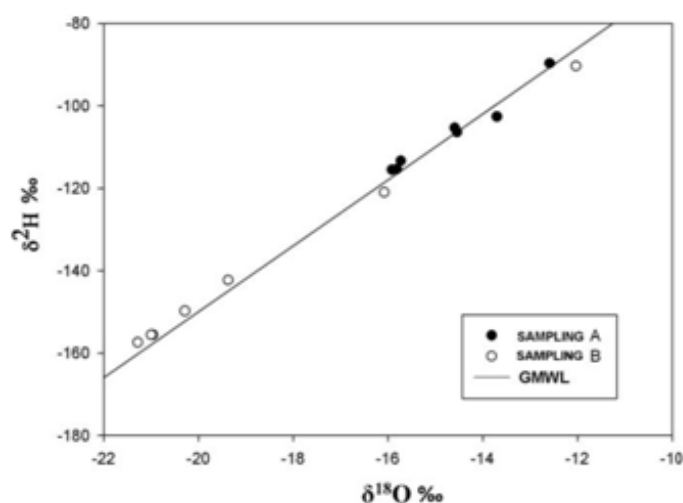

Figure2. *Different precipitation events water stable isotope composition scatter plot. Sampling A: June 26th and sampling B: July 2nd. GMWL: global meteoric water line*

3.2. Isotopic Composition and Hypsometry Analysis

As can be observed in figures 3 to 6, there was no evident relationship between the isotopic composition and the hypsometric differences of each sampling.
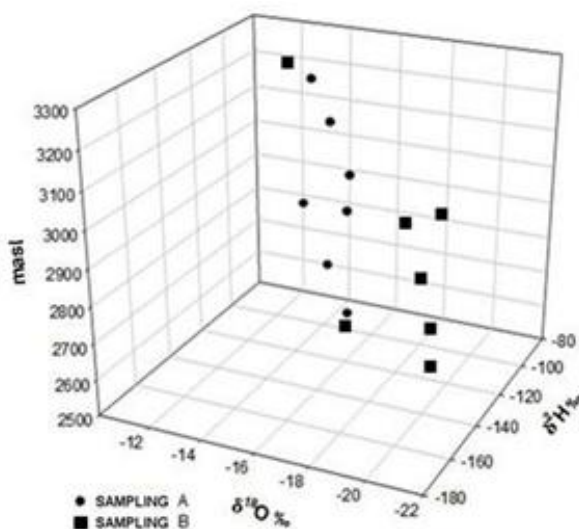

Figure3. *δ^2H and $\delta^{18}O$ composition for each altitudinal level scatter plot*
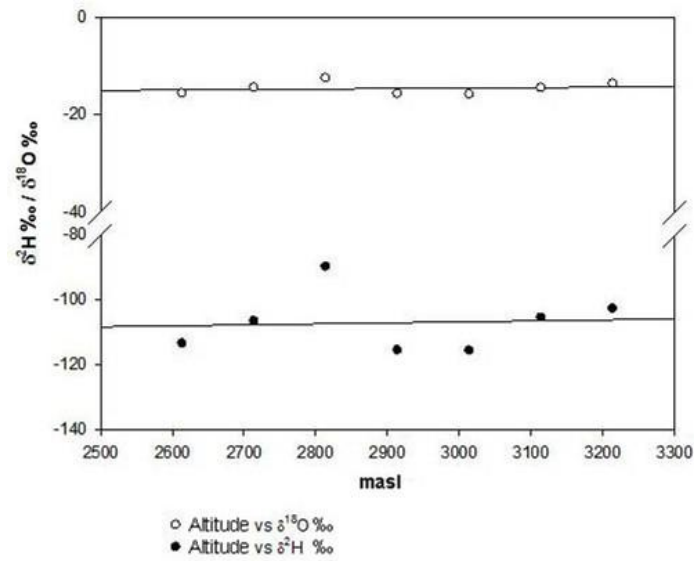
Figure4. *Heavy stable isotopes composition dispersion plot with respect to altitude, for samples collected after the June 25th storm*
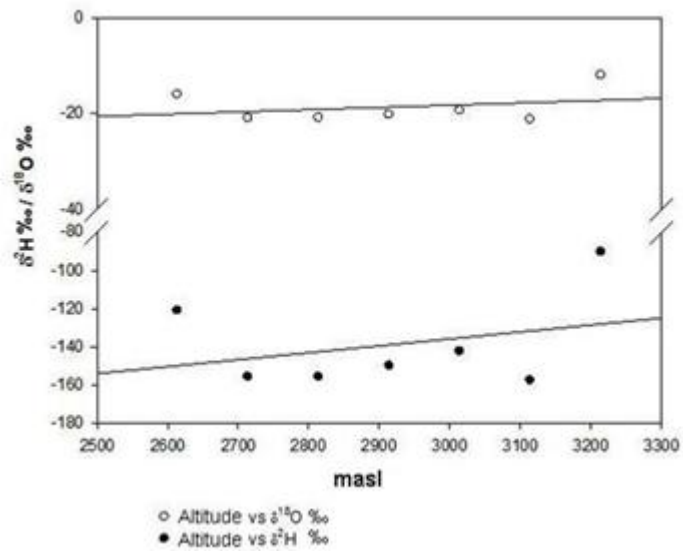

Figure5. *Heavy stable isotopes composition dispersion plot with respect to altitude, for samples collected after the July 2nd storm*
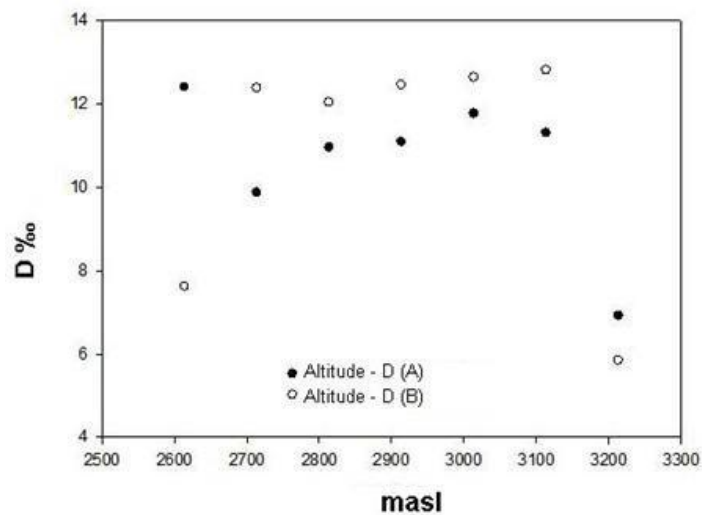

Figure6. *Deuterium excess (D) dispersion plot relative to altitude, for samples collected after the June 25th storm (A) and July 2nd (B)*

3.3. Statistical Analysis

The results of the generalized linear analysis validate this prior assumption. Instead of an altitude effect on the isotopic composition of snow, a significant temporal influence was found. As can be observed in Table 1, the δ^2H and $\delta^{18}O$ values are linked to the different storms events and not to altitude. Significant differences were observed for both, δ^2H ‰ and $\delta^{18}O$ ‰, associated to the storm event date (Date).

Table1. *Generalized lineal model summary for stable isotopes and deuterium excess response variables according to date and altitude factors. Significant variables are marked in bold. The codes represent the p-values as: ** for 0.01 and * for 0.05*

Variable	Estimate	Std. Error	t value	Pr(>|t|)	p
$\delta^{18}O$ ‰					
Altitude	0.002827	0.003517	0.804	0.4385	
Date	**-4.017**	**1.406682**	**-2.856**	**0.0156**	*
R^2 0.44					
δ^2H‰					
Altitude	0.01964	0.02547	0.771	0.45684	
Date	**-31.9257**	**10.18827**	**-3.134**	**0.00952**	**
R^2 0.49					
Deuterium excess					
Altitude	-0.002971	0.003208	-0.926	0.3743	
Date	0.210286	1.283387	0.164	0.8728	
R^2 0.07					

3.4. Air Masses Retro-Trajectory Analysis

The retro-trajectory analysis of the air masses that precipitate in the study area showed different provenance (Fig. 7).
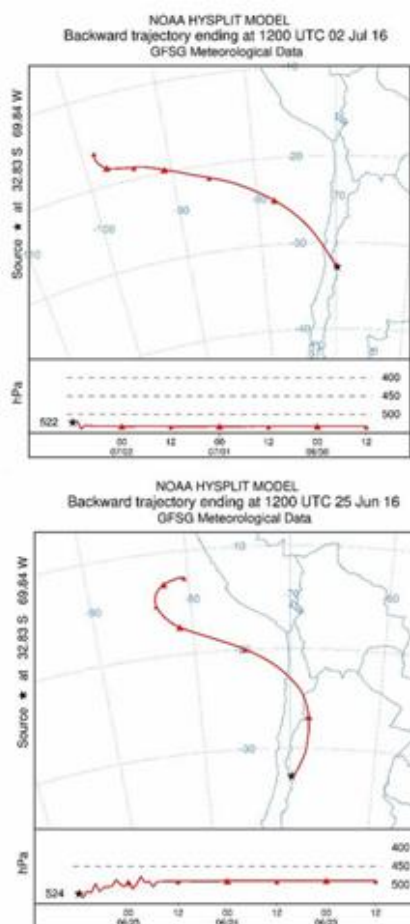

Figure7. *HYSPLIT air masses retro-trajectory analysis of the analyzed precipitations: June 25th (down) and July 2nd, 2016 (upper)*

4. DISCUSSION

Although many studies have found altitudinal effects in the precipitation composition of $\delta^{18}O$ in the Alps, in the order of -0.17 / -0.2 ‰ every 100 m (Mariani et al., 2014; Windhorst et al., 2013; Poage and Chamberlain, 2001; Schotterer et al., 1997; Siegenthaler and Oeschger, 1980), the slope of the altitudinal effect is variable (from 0.1 ‰ to 0.6 ‰ / 100 m), depending on the temperature and isotopic fractionation during condensation, altitude, orographic characteristics, moisture source (Horvatinčić et al., 2005), and the trajectories of the air masses (Aouad-Rizk et al., 2005). In the Cordillera Principal geological province, the stable isotope values of streams and rivers showed a slight altitudinal effect in a previous study, attributed to seasonality and changes in the relative contribution from different water sources to streams (Crespo et al., 2017).

The rain out effect or the preferential discharge of heavy isotopes during the advance of air mass in the windward (Chilean side) is more important than on the studied basin here, located in the leeward side. Once on the leeward side, the altitude decreases as the air masses move eastward, then other effects have more influence on the isotopic compositions. The effects are reflected in this analysis of the isotopic composition of solid precipitation, corresponding to two storm events occurred in the winter season of 2016, where no effects of altitude on snow stable isotope composition were found. The difference in the isotopic composition in each storm event observed, with lower δ^2H and $\delta^{18}O$ values in the later storm event (July 2nd), can be related to the different air mass trajectory as can be observed in the HYSPLIT model (Fig. 7).

5. CONCLUSIONS

According to the isotopic analysis carried out in different storm events along the studied altitudinal gradient, it is concluded there is no significant influence of altitude on the stable isotope composition of snow in this area of the leeward side of Cordillera Principal at 32° S, which feeds the Mendoza River. Even with this space and time limited study, in proportion to the Andes mountain range scale, this work reinforces the use of stable isotope compositions as tracers of different water sources contributions to the upper Mendoza River, as was observed in Crespo et al. (2017).

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SUPPLEMENTARY DATA

Table S1 *Snow stable isotopes composition per altitude and sampling date*

SampleN	Date	Altitude(m)	δ^2H‰	δ^{18}O ‰	d-excess
1	26/06/2016	3214	-102.7	-13.7	6.9
2	26/06/2016	3114	-105.4	-14.6	11.3
3	26/06/2016	3014	-115.6	-15.9	11.7
4	26/06/2016	2914	-115.4	-15.8	11.1
5	26/06/2016	2814	-89.7	-12.6	10.9
6	26/06/2016	2714	-106.4	-14.5	9.9
7	26/06/2016	2614	-113.4	-15.7	12.4
8	02/07/2016	3214	-90.4	-12.0	5.9
9	02/07/2016	3114	-157.4	-21.3	12.8
10	02/07/2016	3014	-142.3	-19.4	12.6
11	02/07/2016	2914	-149.8	-20.3	12.4
12	02/07/2016	2814	-155.6	-21.0	12.0
13	02/07/2016	2714	-155.6	-21.0	12.3
14	02/07/2016	2614	-121.0	-16.1	7.6