Chapter 3

Hydro-Geochemical Water Inputs Identification in Glacierized Basin Hydrology

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Additional information is available at the end of the chapter

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Abstract

Mining activities are usually placed in the upper basin regions, especially in developing countries, with economies that strongly rely on natural commodities. Although glaciers do not occupy a large area of these mountain ranges, they deliver vital water for downstream populations. This is especially relevant during drought periods, when winter precipitation is strongly diminished and ice melt becomes relevant. They are also a key resource for highland wetland ecosystems and paradoxically at the same time for the development of mega-mining projects. Regularly, for environmental impact assessments and relevant public consultations, it will be stated that water from glaciers does not constitute an important source within the basin system, even though this has not been accurately quantified. Different water sources, given by spatial, geological, and hydrological features, can be identified using a combination of ionic and isotopic information from water, thus allowing to establish their proportions downstream, where water from different origins is mixed, and also to track their evolution over seasons. This approach should be useful especially for basins with strong pressures for the exploitation and consumption of water in mountainous basins and also with special relevance for basins with little or no knowledge of their water system and reservoirs.

Keywords: mountain basin, mountain hydrology, natural tracers, glaciers, stable isotopes, water sources

1. Introduction

Numerous mountainous regions of the world are being affected by high-impact extractive activities on the environment, such as mining. These projects are mainly placed in developing countries, where large mining conglomerates can often obtain environmental permits more expeditiously than in developed countries. Apart from the discussion of center and periphery geopolitical condition that began this precarious condition throughout the history of these mostly young countries, there is a general lack of knowledge of the environmental characteristics of the mountainous watersheds, which are necessary to contrast the environmental reports made by corporations.

This institutional fragility condition when granting permits is usually driven by a lack of real environmental valuation, with pillars in null or scarce information of the strategic water resources of the basin.

South America is the home to the longest continental mountain range in the world, the Andes. This narrow and high vertebral column that borders along the subcontinental western side rests on seven countries (Venezuela, Colombia, Ecuador, Peru, Bolivia, Chile, and Argentina) ranging from 10° to 55° S, along most of the latitudinal range of the Southern Hemisphere. This natural wall presents a great interference with the planetary winds, producing a redistribution of the precipitation and evapotranspiration that decants in the formation of the most important rainforest of the planet, the Amazon, toward the east of the massif. Inside the Andes, an accumulation of moisture is generated from the Pacific and Atlantic oceans. These precipitations fall mostly as snow and in the highest places accumulate more than it melts year after year. This condition allows the formation of glaciers and high elevation permafrost, with rock glacier development as characteristic permafrost periglacial environment geoforms. Thus, the snow and glaciers of the South American Andes irrigate these hydrologically allochthonous oases, which hold more than 40% of the subcontinent population, accounting for more than 160 million inhabitants.

The importance of being able to understand these systems in an accessible and reliable way not only responds to the pressures exerted by human activities in the glacial and periglacial mountain environments but also relates to climate change processes that combined with the anthropogenic factor produces an enormous pressure over the balance and sustainability of this vital resource. Long-term climate projections do not present an encouraging picture for the Andean region, as they indicate a warming trend and a greater recurrence of droughts in the coming decades [1–3].

In view of this perspective, it is important for the harmonious development of the population to have accurate information of basin water sources. In addition, it is necessary to recognize with spatial precision the different sources of water from the feeding areas within the basin to the areas where it is used by each inhabitant of the territory. All this, interconnected, serves as a basis for establishing development strategies and providing reliable data for decision-makers [4].

In spite of known ice melting relevance in Andean basins, there is a lack of information of its variations of water supply in space and time. Important questions for the management of water in the territory remain unanswered. Some of the main questions are the following: what is the portion of the total water consumed by the inhabitants that is contributed by each water source (snow, glacial, groundwater) in each part of the basin? Productivity activities, such as cultivation or mining, present different water period need along a year, and this question appears: when is each of these sources inputs more or less important for each kind of water consumption in the basin? Because most of water sources in the basin come from high elevation areas, several of these essential questions remain unanswered. The Andean environment is complex and presents extreme fieldwork conditions for the development of accurate measurements [5]. In addition to this, the different methodologies used to measure the quantity of water do not manage to identify the different water sources and their subsequent variation. For instance, the use of satellite imagery allows to estimate the coverage of snow or glaciers, but not how much of its melt contributes to river's streamflow from the melting of snow or ice, respectively. In the same way, gauges can be installed in every proglacial stream and estimate the ice melt contribution, but, besides the complex field-work scenario, the groundwater influence cannot be analyzed in this projection.

The pressure of the large mineral extractive companies usually makes use of and abuse of this kind of information weakness. In mining environmental impact reports, phrases that refer to the insignificance of the water supplied by glaciers or the periglacial environment are usual. Many studies have demonstrated the ice melting relevance for the total streamflow, especially in dry years. These ice giants play a vital role as damp absorbers in warm and arid years, with higher rates of ablation, which can contribute from 67% [6] to 81% of the total summer flow in the Central Andes (31–37°S) [7]. This process is responsible for the droughts in this region to not reach more critical conditions [8].

The relevance of glacial input to river streamflow can be observed in the stable water isotope (e.g., $\delta^{18}O$) composition from the rivers of the Cordillera Frontal geological province (Argentinean Central Andes), in the very dry years of 2011 and 2012 (**Figure 1**). In this example the rivers were receiving different water source inputs but presented the same isotopical composition as rock glaciers (Rgl).

Faced with this lack of information, the present chapter proposes the use of indirect measurement methodologies to identify the contributions of different water sources to the total basin flow. It seeks to be able to know in an accessible and reliable way the significance of the

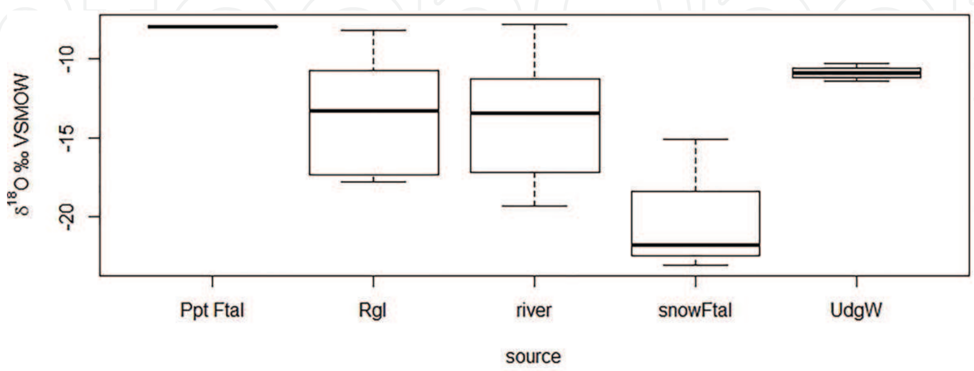

Figure 1. Stable water isotope ($\delta^{18}O$) composition for the different water sources draining the Cordillera Frontal region (32° 56′ S; 69° 22′ W). Ppt Ftal, total precipitation; snowFtal, snowfall samples during storm events; Rgl, rock glaciers; UdgW, groundwaters (Source: personal elaboration).

contribution from each water source and the opportunity to deliver it in space and time using water natural tracers. These are water stable elements with different proportions in each different water source, without significantly changing their properties over time. This property can be analyzed and performs traceability during its journey in the hydrological cycle. In this chapter we will focus on the interpretation and use of two major types of natural water tracers: water stable isotopes and major ions.

This could represent an important tool for policy-makers and the basin's sustainable development in the present and future sociopolitical and climate scenarios.

2. Water source differentiation and quantification using natural tracers

Inner-basin geological differences, in combination with climatic variables and sediment contact time through the basin, provide an ionic and isotope differential composition of natural waters [9–12].

Consequently, this chapter will focus in showing a combination of stable water isotopes and ionic tracer analysis, allowing the readers to identify surface water that originates in different sources like water released from ice bodies, groundwater, rain storms, or snow catchments.

2.1. Ionic tracing

From the universe of water compounds, in this section, we will focus on major ions, which are usually analyzed. Total salinity, measured by electrical conductivity, will also be discussed.

In **Figure 2**, an example from an arid mountain basin (the upper Mendoza River basin) can be observed. The geological map of the area is composed from different geological provinces represented in different mountain ranges, named as Cordillera Principal, Cordillera Frontal, and Precordillera, from west–east direction, respectively. As usually occurs in mountain areas, because of the geological differences from each mountain range, water-draining these geologically different basin areas is expected to present different compositions of minerals and ionic chemistry (**Figures 3** and **4**).

In this case, the samples were taken at different sites in the basin, in 500 cc sterile plastic bottles. For these samples, electrical conductivity and the following major ions, bicarbonate (HCO_3^-), sulfate (SO_4^{-2}), chloride (Cl^-), calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^+), and potassium (K^+), were analyzed.

As can be observed in **Figure 3**, the geological differences expressed different ionic quantities in the rivers draining the different areas, and the total salinity is like a summary of this process.

For the ionic composition, in a more graphical representation with a Piper diagram (**Figure 4**), a sulfated calcium and magnesium composition for the samples extracted in the Cordillera

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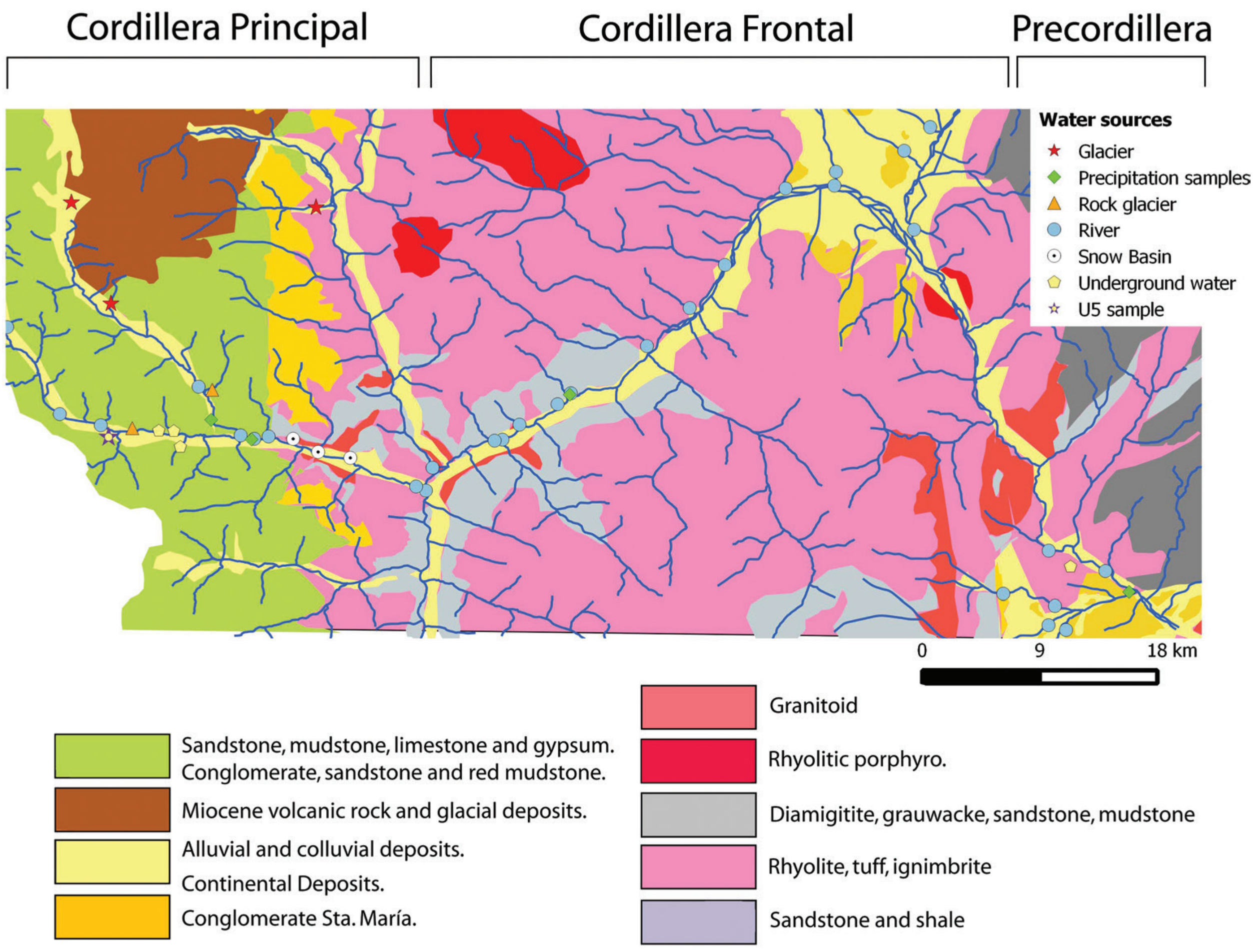

Figure 2. Upper Mendoza River basin (32° 50′ S; 62° 45′ W) geological map (Source: personal elaboration).

Principal and calcium and magnesium bicarbonated for those of the Cordillera Frontal geological province can be seen. Precordillera presents bicarbonated sodium waters mostly. The influence of the petrographic characteristics from the Cordillera Principal, dominating with the presence of gypsum and marking the composition of the Mendoza River waters (mix), which is formed by all the tributaries along the whole studied basin can also be observed.

2.2. Isotopical tracing

Isotopes are atoms of the same element that possess different neutron numbers in its nucleus, presenting equal atomic number but different mass numbers. The differences in mass generate a different behavior in physically reactions. The mass difference between the atomic nuclei is expressed in different reaction rates, because the isotopically heavier molecules have less mobility, resulting in a lower diffusion rate and a lower frequency of collision with other molecules. This derives in a lower possibility of physical reactions, a situation where light molecules react more frequently. This partitioning of isotopes between two substances or two phases of the same substance with different isotopic contents is known as isotopic fractionation [13].

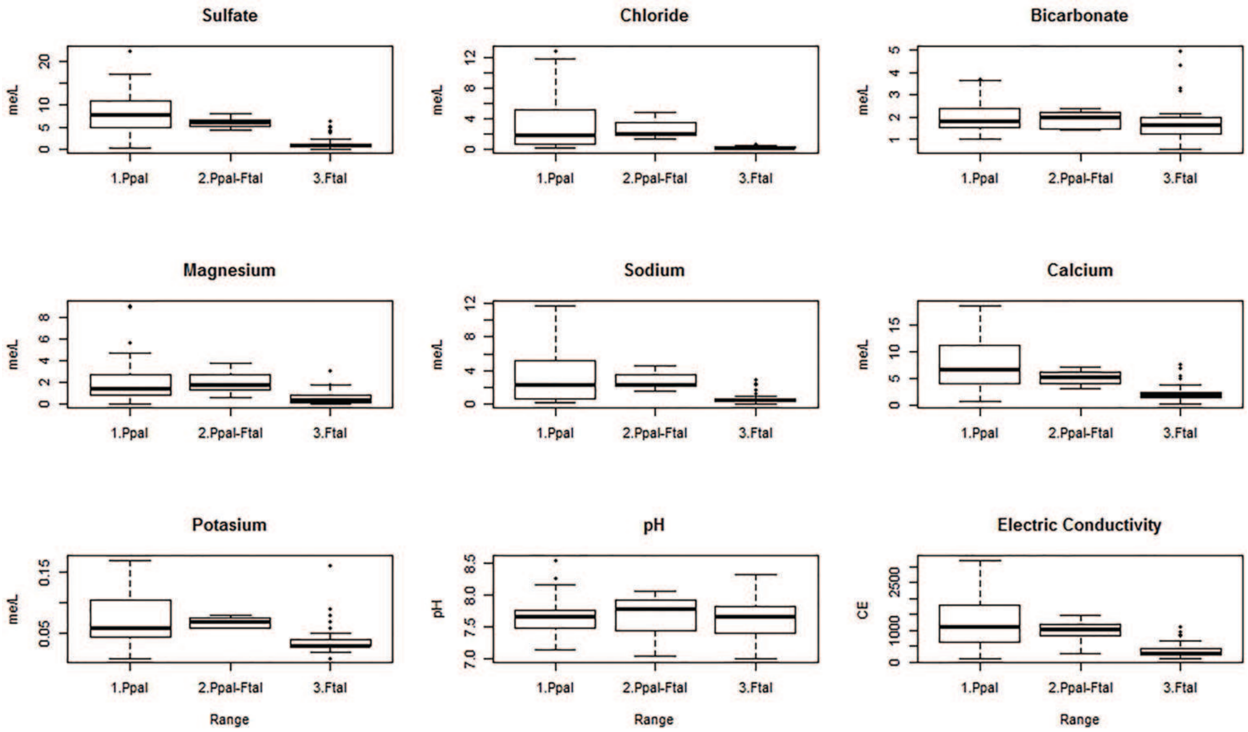

Figure 3. Different mountain ranges' major ions, pH, and electrical conductivity water composition. (1) Ppal, refers to the Cordillera Principal geological province; (2) Ftal, to the Cordillera Frontal, and (3) Ppal-Ftal, to the Mendoza River where the waters incoming from Cordillera Principal and Frontal are mixed (Source: [12]).

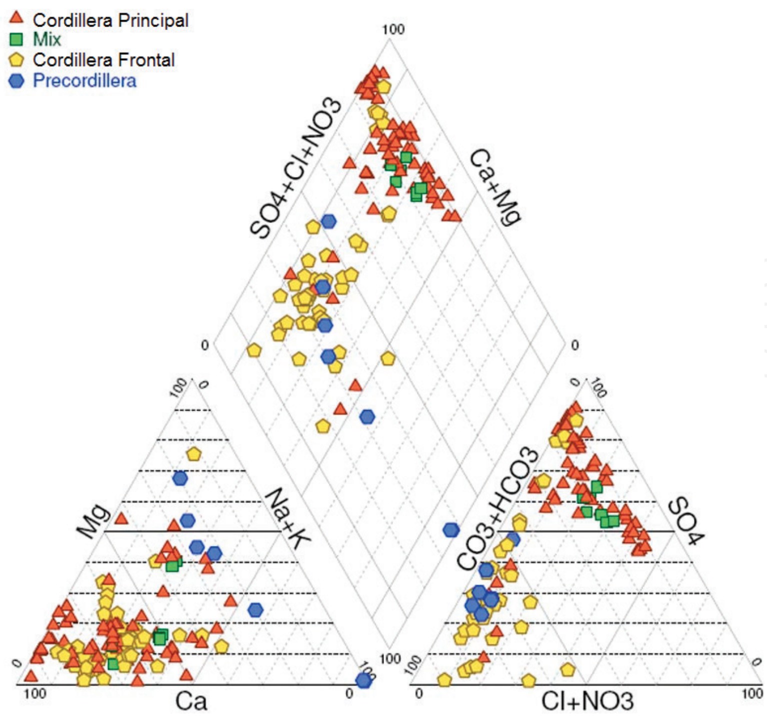

Figure 4. Different geomorphological units within the Mendoza River basin and water ionic composition Piper diagram (Source: [12]).

In order to express the contents of these less abundant isotopes, working standards are used for the measurement of the called δ values. Also, to facilitate interlaboratory comparisons, δ values are scaled to internationally accepted standards. Because water is composed by hydrogen and oxygen, and both present heavy stable isotopes, we will focus on these ones. The hydrogen heavy stable isotopes are deuterium and tritium. Oxygen presents two stable isotopes: ^{18}O and ^{17}O. This chapter will be focused in the more abundant and used: the deuterium ^{2}H and the ^{18}O [14]. The differential composition of the different water sources arises from this explained isotopic partitioning.

The standard commonly used to report the values of $\delta^{18}O$ and $\delta^{2}H$ is the VSMOW (Vienna Standard Mean Ocean Water). Then, the values are expressed in $\delta^{18}O$ y $\delta^{2}H$ ‰, according to Eq. (1):

$$\delta_{VSMOW} = \frac{R_{sample} - R_{VSMOW}}{R_{VSMOW}} * 1000 \qquad (1)$$

In this way, when ocean water (which is considered to have an average δ_{VSMOW} value equal to zero) evaporates, it will generate a heavy isotope depletion (which evaporates proportionally less). When moisture is then transported by winds into the continent, water will be discharged as precipitation fractionating preferentially heavy isotopes along its path; therefore, the water vapor will become increasingly depleted on the heavy isotopes. This will leave a characteristic composition in different water sources, depending on the effects that modify this fractionation (continental effect, latitude, altitude, temperature, etc.). The resulting isotopic composition can then be analyzed and its origin and evolution traced [12, 13, 15], as can be observed in **Figure 5**.

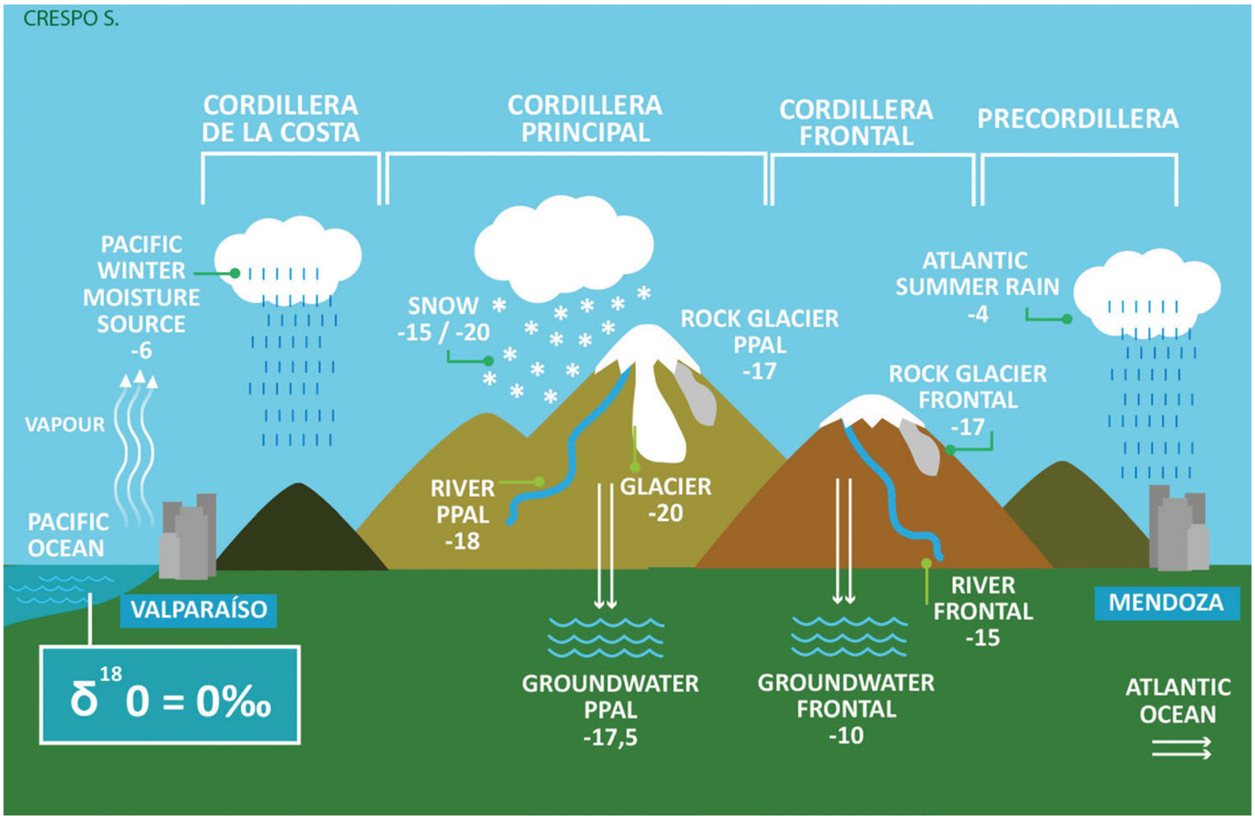

Figure 5. Water $\delta^{18}O$ evolution content in the hydrological cycle (Source: personal elaboration).

In the basis that environmental factors (such as geological and topographical settings, climate, isotope fractionation processes during cloud formation and precipitation) will imprint the stable water isotope composition, researchers have been using this isotopic finger print to identify the water source draining processes to rivers around the world.

Summarizing, isotopic compositions from the different water sources are affected by soil-atmosphere exchange processes, such as precipitation, melting, evaporation, and sublimation [15], which will change according to the altitude, temperature, isotopic composition of the moisture source, and surface characteristics that affect the energy balance of the evaporation processes.

In the case of surface water sampled from the different geomorphological units in a mountain basin (in this case, Cordillera Principal, Cordillera Frontal, and Precordillera mountain ranges), when the co-isotope (δ^2H and $\delta^{18}O$) composition is plotted (**Figure 6**), a significant increase in heavy isotope concentrations as altitude decreases (going east, from the Cordillera Principal to the Precordillera) is clearly observed. Isotopic composition differences between different water sources (glaciers, rock glaciers, groundwater, snow, or rivers) are also observed.

Another useful tool derived from isotopical tracing is the "deuterium excess." Under different conditions than 100% atmospheric humidity, the fractionation rate of hydrogen is higher than oxygen heavy isotopes. This difference in fractionation rates is expressed as the "deuterium excess" and is calculated according to Eq. (2):

$$d = \delta^2 H - 8 * \delta^{18} O \quad (2)$$

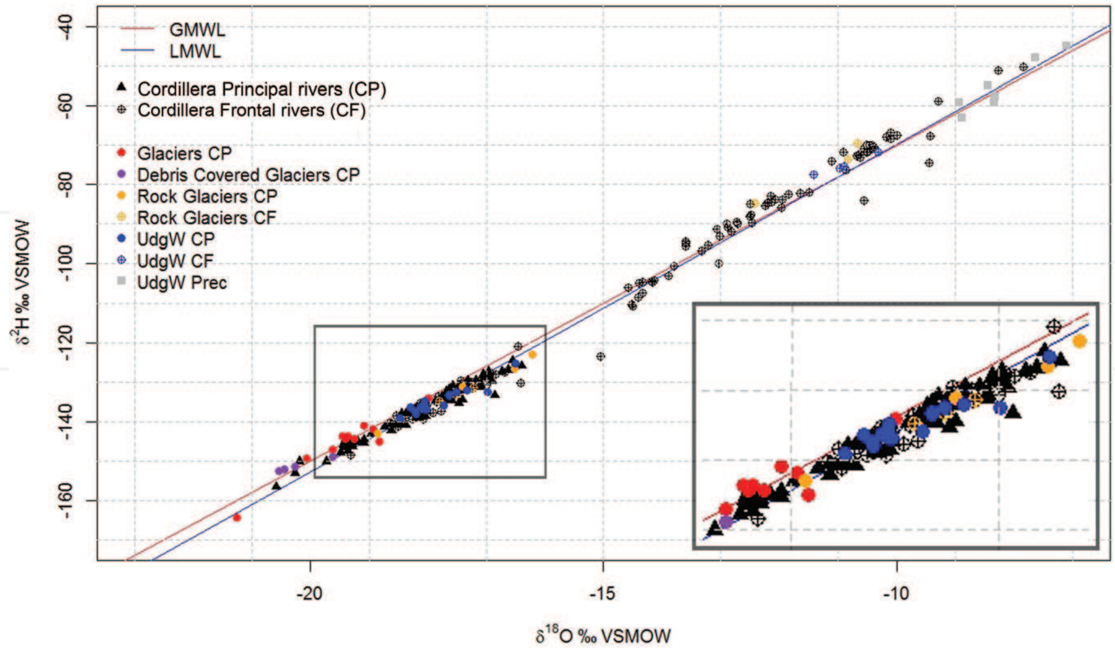

Figure 6. Dispersion of the stable isotope values of water samples analyzed in the Mendoza River basin. The blue line represents the Local Meteoric Water Line (LMWL), following the equation: $\delta^2H = 8.29\ \delta^{18}O + 13.13$; $R^2 = 0.99$. The red line represents the Global Meteoric Water Line, (GMWL) (15) (Source: [12]).

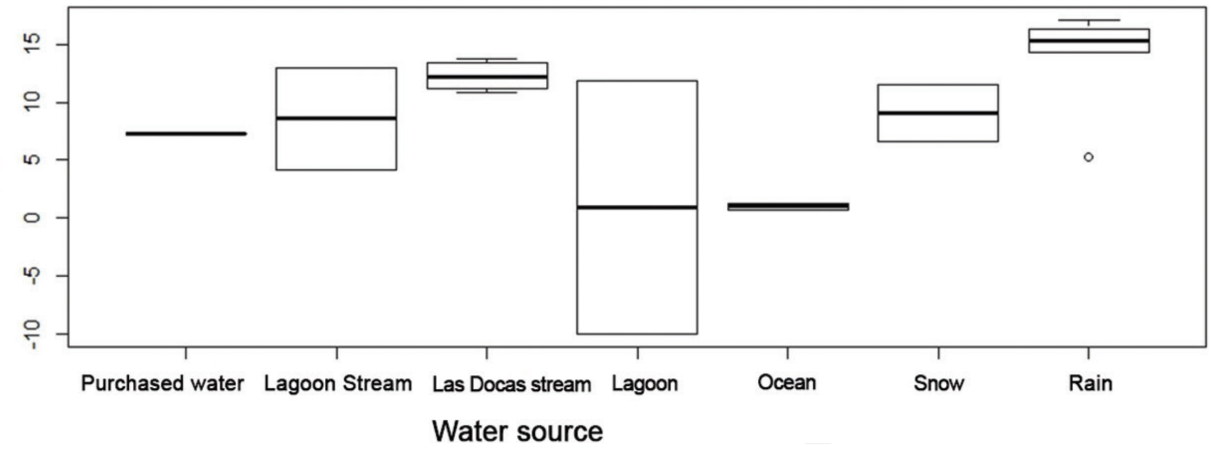

Figure 7. Different water source deuterium excess values in Las Docas beach area, Central Chile (33° 8′ S; 71°42′ W). QLR stream refers to a seasonal stream inside Las Docas region. Lagoon stream refers to the tributary stream feeding the estuarine lagoon (Lagoon) (Source: personal elaboration).

Since $^{18}O/^{16}O$ variations in precipitation were observed [16], Craig [17] described the Global Meteoric Water Line, and Dansgaard [18] introduced the deuterium excess concept, many decades have passed and the stable water isotope applications have developed rather fast. Currently, stable isotopes are widely used by scientists from many different fields to provide information about the origin and geochemical history of water.

This value is very important to determine different evaporation processes, such as by water stagnation and evaporation. In **Figure 7** an example of water sources (in this case in Las Docas region, Central Chile) is presented. Deuterium excess values (d‰) from different streams, rain, and ocean, which fed the estuarine lagoon, show evident differences. The lower deuterium excess values of the lagoon are explained by evaporation processes. The hydrogen isotopes are more affected by the evaporation process than the oxygen heavy isotopes, by the explained mass difference resulting in different fractionation inertias.

Sometimes, two or more water sources cannot be distinguished significantly via δ^2H, $\delta^{18}O$, or ionic determination. In this case, the differential signature can be detected using the deuterium excess value. In **Figure 8**, a graphic example is presented where it was possible to significantly differentiate uncovered glaciers (nr. 1) with snow basins (nrs. 7 and 9) through the differential evaporation condition expressed in the deuterium excess value for each source.

2.3. Combined ionic and isotopic composition analysis

Using the chemical and stable water isotope characterization previously presented, a statistical analysis could be carried out to investigate if any significant differences can be identified and thus to strengthen the information that can be provided in order to identify different water sources. As it was observed for the Mendoza River basin (**Figures 4**, **6**, and **8**), the different tracer composition allows the contribution identification from different geographic origins in space and time, considering the characteristic composition of each type of water source in each subbasin and, from there, estimates the proportion and moment of water delivery in a basin [12].

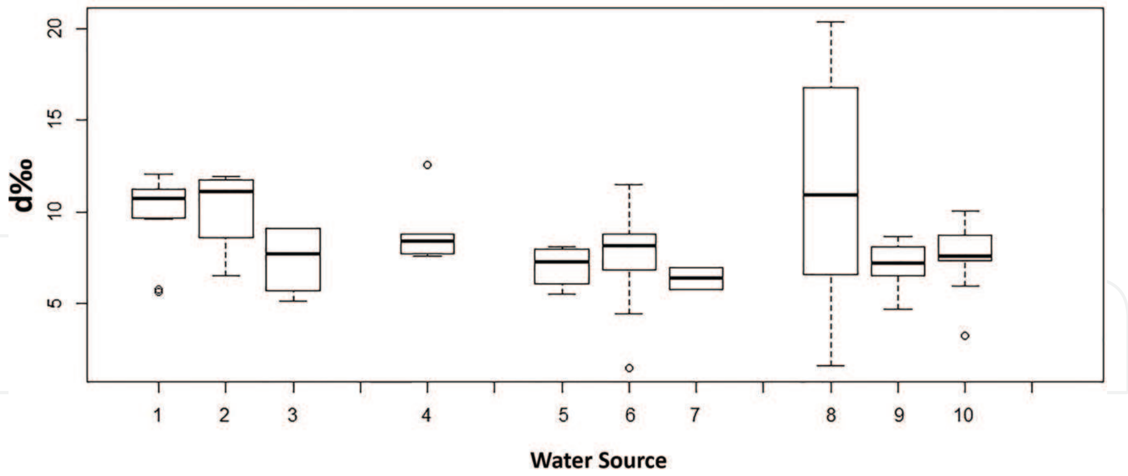

Figure 8. Different water sources (in numbers) deuterium excess values (D‰) in the Cordillera Principal mountain range area, upper Mendoza River basin. (1) glacier, (2) debris-covered glacier, (3) debris-covered glacier and rock glacier, (4) total precipitation, (5) rock glacier, (6) rivers and streams, (7) "Valle Azul" stream in winter and spring, (8) snow, (9) "Los Puquios" stream in winter and spring, (10) groundwater (Source: [4]).

A combination of both, ionic and isotopic compositions, can reveal river behaviors along a year. In this case, a simplification thought a principal components analysis (PCA) can be a useful way. As can be seen in **Figure 9**, the first dimension of a principal component analysis (PCA), related to ion chemistry, separates groundwater from snow and ice bodies. The second dimension, related to stable isotopes, separates the snow and the different types of ice bodies (snow and rock glacier from uncovered or debris-covered glaciers). The temporal evolution of the different rivers along the main dimensions of the PCA shows a movement along the stable isotope axis, which is considerable in summer compared to autumn in several rivers. Saline

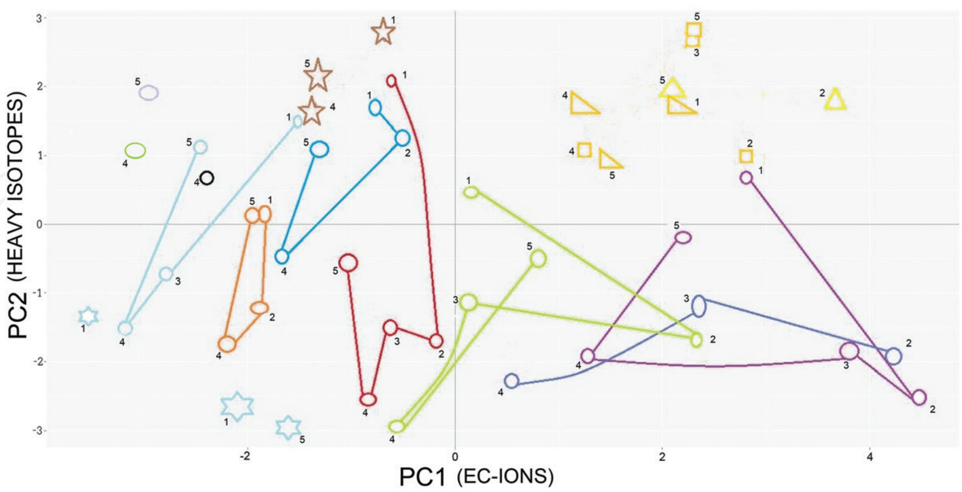

Figure 9. Stable isotopes and salts of water samples from the Mendoza River basin principal components analysis (PCA) plot. The behavior (marked by the dominance of the contribution of glaciers, groundwater, or snow) of the different subbasins that contribute to the Mendoza River (marked by the different rivers with the lines in different colors), throughout the seasons of the year. The number 1 corresponds to summer, 2 autumn, 3 winter, 4 spring, and 5 to the summer of the following year. In the upper left margin is the resulting characteristic of rock glaciers (brown stars) and snow precipitation (green and black circles). In the upper right of the groundwater (yellow rectangles and triangles) and, in the lower left, the characteristic features of glaciers (blue stars) (Source: [12]).

concentration is observed in autumn, indicating the contribution of water with greater contact with sediments (groundwater). The observed changes from autumn to spring are observed in the ion dilution dimension and then again become a predominantly snow contribution in early summer. In this case, it was a temporal lagoon detected (purple circle in **Figure 9**). The water source that had been feeding the lagoon was unknown, because it could be a snowmelt or a groundwater water source origin. As can be observed (**Figure 9**), after the PCA analysis, the snowmelt provenance of the water filling this temporal small lagoon was inferred [12].

2.4. Water source input quantification

In order to quantitatively estimate the relative contributions from each type of water source to a river flow, an end-member mixing analysis (EMMA) [19] could be performed based on the chemical determinations previously explained.

In this way, the equation for proportions *(f)* of river inputs composed by three components (*C:* snow or rock glacier, glacier, and groundwater) requires the use of two tracers (ions and isotopes), and the ratio of each source is calculated according to the following set of equations (Eqs. 3 to 8):

$$1 = f_1 + f_2 + f_2 \tag{3}$$

$$C_1^1 f_1 + C_2^1 f_2 + C_3^1 f_3 = C_t^1 \tag{4}$$

$$C_1^2 f_1 + C_2^2 f_2 + C_3^2 f_3 = C_t^2 \tag{5}$$

where f is the discharge fraction and C is the component concentration. The subscripts refer to the components and superscripts to the tracers.

And, finally

$$f_1 = \frac{(C_t^1 - C_3^1)(C_2^2 - C_3^2) - (C_2^1 - C_3^1)(C_t^2 - C_3^2)}{(C_1^1 - C_3^1)(C_2^2 - C_3^2) - (C_2^1 - C_3^1)(C_1^2 - C_3^2)} \tag{6}$$

$$f^2 = \left(\frac{(C_t^1 - C_3^1)}{(C_2^1 - C_3^1)}\right) - \left(\frac{(C_1^1 - C_3^1)}{(C_2^1 - C_3^1)}\right) f^1 \tag{7}$$

$$f_1 = 1 - f_1 - f_2 \tag{8}$$

For three components and two tracer models, as it was the example, the mixing spaces are defined by the two tracers (e.g., isotopic composition and electrical conductivity). If they are graphed, the three components must form the vertices of a triangle, and all the samples of the river must be framed by the triangle. If this standard is not met, the tracers are not conservative, or there may be contributions from other sources not characterized (**Figure 10**).

In this example, the relative contribution from each water source for the Cuevas River in February 2014 is presented in **Table 1**.

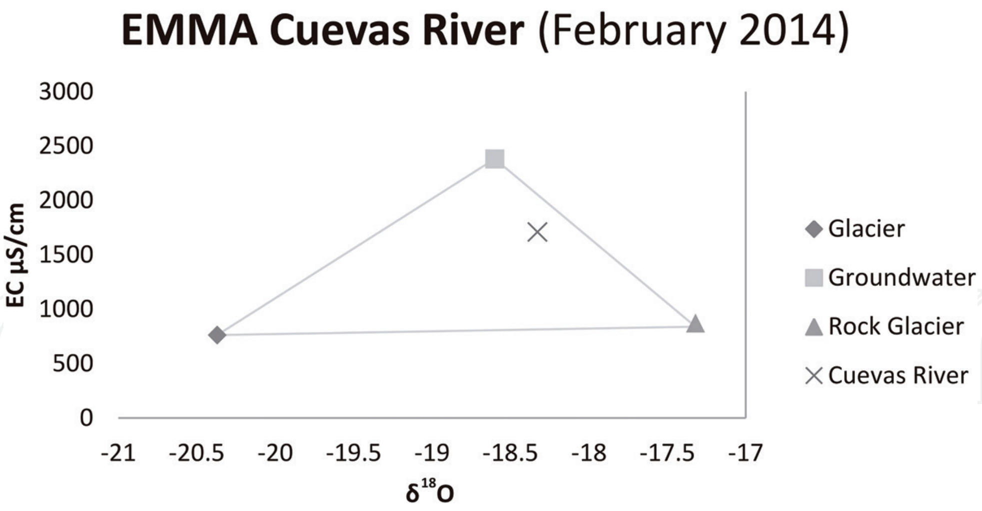

Figure 10. Scatter plot showing the isotopic and average electrical conductivity (EC) compositions for the different water sources that contribute to the Cuevas River in February (Source: [4]).

Water source	Glacier	Groundwater	Rock glacier	Other	Total
Water source contribution (%)	9	56	34	1	100

Table 1. Percentage contribution from different water sources to the Cuevas River along February 2014 (source: [4]).

3. Conclusions

In water management, a lack of knowledge about the natural water source contribution variability in different periods of the year exists, which is critical at any time when it is necessary to maintain the water balance between supply and demand in a certain territory. Within the large basins, there is still a great complexity for the determination of water sources in high elevation areas. This is also a challenge for small basins, where water systems can be even more fragile. The difficulty lies in the fact that in high-altitude areas with different water sources, there are variations in the contribution proportion from each kind of water source, along each season of the year. Among them, we can count the presence of glaciers, snow, total precipitation, wetlands, groundwater, and permafrost, where all can contribute to the runoff and recharge aquifers in territories located in lower areas within the basin. As could be observed in this chapter, using chemical tracing through natural tracers represents a reliable way to distinguish and quantify the different water sources input in a river.

Society is the main target of any water basin analysis, and, based on it, territorial prospecting can make important contributions in the estimation of impacts and in the mitigation infrastructure design. In this context, this chapter focuses on the determination of water sources in high-altitude areas using natural tracers, which can be very useful for the communities that inhabit the basins in mountain areas. The spatial and temporal distribution data of the water supply's main components is fundamental for the hydrological resource use and distribution planning among the basin's different social actors. These tools could be relevant to water supply projections and water demand regulations when analyzing the water source bail in upper basin areas, as a consequence of precipitation reduction and temperature increase in high elevations, which, for example, has resulted in a generalized retreat of the glaciers along the Central Andes [8, 20–22]. It is estimated that these glaciers' fronts and areas' negative variations are largely due to the rise of the 0°C isotherm in the region [23]. Also, when some corporations deny any specific water source contribution relevance, these tools can provide a good exploration analysis to determine their water contribution.

Recently, between 2010 and 2015, the Andes region between 29° and 35°S experienced the longest drought in the instrumental record [3]. This extraordinary event has occurred in the warmest decade of the last 100 years and apparently has no analogies in the last millennium, according to paleoclimatic reconstructions of this area [3]. The long-term climate projections also do not present an encouraging picture for this region of the Andes, since they indicate a tendency to warming and a greater recurrence of droughts in the coming decades [1, 3, 24].

In view of the worrying future perspective that is coming for this region (and others) in terms of its reduction of strategic water resources, it is vital to know in detail the behavior of the different water sources associated with climate variability. In this chapter we have shown the different contribution along time and space from different water sources, which can be key information for the development of reservoir infrastructure and water distribution networks, generation of water supply, and distribution models for different uses, in addition to other adaptation plans aimed at specific sectors of the population.

The use of ionic and isotopic tools, together with traditional hydrological and climatic data, can allow the creation of new information and early warning systems to reduce the risk of droughts and floods, among other applications that will modernize the way we guide decision-making in complex climate dynamic mountain basins. Besides this, extending these tools to other areas of the landscape, such as the foothills, lowlands, and valleys, will be useful to recognize and quantify changes in isotopic signatures in space and time. The knowledge of this water information can be considered analogous to the knowledge of the circulatory system in living organisms, because it is vital to diagnose the functioning and health of the ecosystems that feed on this resource in different basin zones. This information will favor the different water source feature identification from the feeding areas within the basin to the areas where it is used by each inhabitant of the territory.

In summary, the development of new geographic and temporal information systems using chemical and isotopic tools is of fundamental importance for water distribution, flood, and drought damping infrastructure planning scenarios. Interconnected to other environmental parameters, it will serve as a basis to establish development strategies and provide information for decision-making in areas that depend on mountain hydrology and its complex network of water sources that supply the territory.

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A. Appendices and nomenclatures

Glacier (discovered and covered): permanent ice body generated on the ground by snow and/or ice recrystallization due to the compaction of its own weight, without or with significant detrital coverage, which is visible for more than 2 consecutive years, with movement evidence or not. Glaciers can have different morphologies.

Groundwater: this term is used here to describe indistinctly (unless clarified) to spring waters and can represent waters of the soil matrix or from deep water and old sources.

Periglacial environment: this term is used to describe the climate and the geomorphic processes of the peripheral areas to the discovered ice and to those distant zones to these also without direct relation with glaciers but with the low temperatures, with permanently frozen soils and even with those zones with short period, seasonal, or daily freezes. In many cases the ice can be trapped and preserved under natural conditions for a long time, thus constituting the decisive element of the cryogenic environment [25].

Permafrost: soil that remains frozen for 2 or more consecutive years.

Rock glacier: frozen debris body and ice with evidences of movement by gravity and permafrost plastic deformation, whose origin is related to the cryogenic processes associated with permanently frozen ground and with underground ice or with ice from uncovered and debris-covered glaciers.

Snow basin: refers to a basin where the snow precipitation is the very major water source.

Total precipitation: refers to the meteoric water precipitated at any state (solid or liquid).

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