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Vertical variation in the amplitude of the seasonal isotopic content of rainfall as a tool to jointly estimate the groundwater recharge zone and transit times in the Ordesa and Monte Perdido National Park aguifer system, north-eastern Spain

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HIGHLIGHTS

GRAPHICAL ABSTRACT

- · Amplitude of seasonal isotopic composition of rainfall depends on elevation.
- · Moisture generating rainfall at the PNOMP comes from a main source.
- The flow system tends to a better mixing the longer the system transit time is
- · The aquifer recharge zones located at elevations between 2600 1950 m a s l
- Short transit times in agreement with the karstic nature of the aquifer system

 Z_{2}

Elevation and



Seasonality

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ABSTRACT

The time series of stable water isotope composition relative to meteorological stations and springs located in the high mountainous zone of the Ordesa and Monte Perdido National Park are analyzed in order to study how the seasonal isotopic content of precipitation propagates through the hydrogeological system in terms of the aquifer recharge zone elevation and transit time. The amplitude of the seasonal isotopic composition of precipitation and the mean isotopic content in rainfall vary along a vertical transect, with altitudinal slopes for δ^{18} O of 0.9%/km for seasonal amplitude and -2.2%/km for isotopic content. The main recharge zone elevation for the sampled springs is between 1950 and 2600 m a.s.l. The water transit time for the sampled springs ranges from 1.1 to 4.5 yr, with an average value of 1.85 yr and a standard deviation of 0.8 yr. The hydrological system tends to behave as a mixing reservoir.

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Seasonal isotopic amplitude Transit time Recharge Alpine hydrology Karst hydrology Parque Nacional Ordesa y Monte Perdido

1. Introduction

In hydrological sciences, the stable water isotopes of precipitation have been widely used as natural tracers, taking advantage of the different processes affecting the atmospheric water vapor since it is generated until it produces precipitation (Gat, 1996; Mook and De Vries, 2000; Liotta et al., 2008). In most cases, these processes are affected by temperature-driven isotope fractionation (Dansgaard, 1964; Yurtsever and Gat, 1981; Rozanski et al., 1993; Araguás-Araguás et al., 2000; Mook and De Vries, 2000; Gonfiantini et al., 2001; Liebminger et al., 2006a; Stumpp et al., 2014, among others). The altitude effect (Mook and De Vries, 2000; Rowley et al., 2001; Poage and Chamberlain, 2001; Liotta et al., 2006; Fiorella et al., 2015 and references therein) and the seasonality effect (Gat, 1996; Mook and De Vries, 2000; Jódar et al., 2016) are the most relevant processes in mountainous zones.

The altitude effect refers to the empirical relationship between the isotopic content of rainfall (δ_{in}) and elevation (*Z*), which is described by the "altitudinal isotopic water line". This effect is generated by thermal air stratification enhanced by atmospheric advection, as the air masses climb up along the slopes of high mountains. The forced uplift generates an adiabatic expansion of the advected air parcels that cool them. This generates an orographic precipitation process in which vapor condensation increases (i.e. cloud droplets) and consequently precipitation is removed from the air parcel. In other words, the forced air uplift generates a Rayleigh cooling process (Gat, 1996) that fractionates the isotopic content of rainfall as the air parcel climbs up along the slopes of the mountain. As a result, the hydrogen and oxygen heavy isotope contents of precipitation decrease with increasing elevation (water becomes isotopically lighter). The isotopic lapse rate (i.e., depression of isotopic δ_{in} values per unit increase in elevation), even if steady in the long-term, is not stationary (Andreo et al., 2004; Liebminger et al., 2006b; Fernández-Chacón et al., 2010; Kern et al., 2014). It may be affected by seasonal variations of temperature because the altitude effect is a temperature-driven fractionation process.

The isotopic content of a water sample (m) is commonly given relative to a standard (s) and expressed as $\delta = (R_m - R_s) / R_s$, where R is the ratio between the rare and the abundant isotope concentrations, which for water refers to oxygen (${}^{18}O/{}^{16}O$) and hydrogen (${}^{2}H/{}^{1}H$). δ_{in} can be used as a groundwater tracer in hydrological studies (Clark and Fritz, 1997; Gat, 1996; Kendall and McDonnell, 1998; Lee and Krothe, 2001). Once the altitudinal isotopic water line has been locally characterized, then the δ_{in} values can be used to identify the aquifer recharge areas and their hydrogeological connection with the discharging springs (Lambán, 1998; Lambán and Custodio, 1999; Paternoster et al., 2008; Parisi et al., 2011; Liotta et al., 2013; Vallejos et al., 2015; among others) if there is a well-defined recharge zone. Otherwise, when recharge is distributed over a wide range of altitudes, there is a slope effect (Custodio, 2010; Custodio and Jódar, 2016). In this case, the deduced altitude has not an easy meaning as it does not necessarily coincide with a centroid, as flow pattern geometry and recharge distribution affect results.

The seasonality effect refers to the periodic oscillations of the isotopic composition of precipitation generated by the seasonal changes of temperature. The seasonal isotopic content in infiltrating precipitation enters as an input tracer signal in the hydrogeological system along with recharge. This signal is buffered and delayed with respect to the input tracer signal as it propagates through the hydrogeologic system. The differences between the input and the output tracer signals (i.e. amplitude dampening and time shift) at the outlet of the system allow the estimation of both the system transit time (τ) and the system transit time distribution (McGuire et al., 2002; Reddy et al., 2006; Kabeya et al., 2007; Stumpp et al., 2009; Niinikoski et al., 2016; among others). The transit time distribution provides a primary description of the hydrological system behavior. It is usually inferred using lumped parameter models (LPM) (Małoszewski and Zuber, 1982; Amin and Campana, 1996; Leibundgut et al., 2011; Jódar et al., 2014). As LPMs do not require detailed hydrological knowledge of the physical system, they are especially well suited to study hydrological systems in karst and complex fractured zones, especially in mountainous areas where an internal detailed description of the most relevant hydrological features is often not available.

In mountainous zones, the altitude and seasonality effects are closely related given by their common dependence on temperature. The topographic altitudinal differences generate a vertical temperature gradient $\nabla_{Z}T$ that allows the Rayleigh cooling process to fingerprint the average altitudinal isotopic water line $\overline{\delta_{in}}(Z)$, which is usually assumed as stationary for average values. The seasonal variation of temperatures induces a seasonal variation in the isotopic content of rainfall along the vertical transect in which $\overline{\delta_{in}}(Z)$ exists. As a result of seasonality, the temporal dependence of the isotopic content of rainfall for a given elevation Z_i can be expressed as a sinusoidal function, with amplitude A_{in} and a mean value that coincides with $\overline{\delta_{in}}(Z_i)$. The spatial invariance of A_{in} is implicitly assumed in the numerous studies available in the bibliography. Given that τ is obtained as a function of the amplitude dampening at the outlet of the hydrogeological system (Małoszewski and Zuber, 1982; McGuire and McDonnell, 2006), the assumption of a constant A_{in} allows the estimation of the hydrogeological system transit time τ without previously characterising $\overline{\delta_{in}}(Z)$. Nevertheless, in mountainous zones, A_{in} may depend on elevation (Jódar et al., 2016). The resulting vertical gradient of A_{in} (i.e. $\nabla_z A_{in}$) makes the τ estimation to be dependent of the previous characterization of $\overline{\delta_{in}}(Z)$. The hydrological implications of $\nabla_z A_{in}$ have not been addressed yet.

The objective of this work is twofold: 1) to present a methodological approach to account for $\nabla_z A_{in}$ in the jointly estimation of $\overline{\delta_{in}}(Z)$ and τ , and 2) to apply the methodology to the high-altitude karst aquifer system of Ordesa and Monte Perdido National Park (PNOMP), Spain. This is in order to explain the relationship between meteoric water recharge and the groundwater system in terms of the altitude of recharge and the transit time associated to the sampled springs. This will advance the fundamental understanding of the governing hydrological processes in the aquifer system of the PNOMP.

2. The study area

The PNOMP is located in the central sector of the Pyrenees (Fig. 1), which is the most important mountain chain of the Iberian Peninsula. The maximum altitude in the PNOMP corresponds to the Monte Perdido peak, $3355 \text{ m} \cdot \text{a.s.l.}$ (above sea level), the third highest peak of the entire Pyrenean range. The lowest point, at 689 m $\cdot \text{a.s.l.}$, is in Fuen dero Baño spring (site 22, Fig.1, Table 1).

From a climatic point of view, according to the Köppen-Geiger classification (Peel et al., 2007), the PNOMP has a cold climate with a dry season, with mild and cool summers and significant altitudinal variations. At the Fanlo-Góriz meteorological station (P1, Table 1), which is located at 2200 m·a.s.l., the mean annual temperature is 4.9 °C and

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